

This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

- + *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.
- + Refrain from automated querying Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.
- + *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.
- + Keep it legal Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at http://books.google.com/





•

•

.

.

•







A TEXT-BOOK ORGANIC CHEMISTRY

RICHTER
---ANSCHÜTZ
--SMITH



VOLUME I OF THIS WORK INCLUDES THE CHEMISTRY OF THE ALIPHATIC SERIES

VICTOR VON RICHTER'S

ORGANIC CHEMISTRY

OR

CHEMISTRY

OF THE

CARBON COMPOUNDS

EDITED BY

PROF. R. ANSCHÜTZ

UNIVERSITY OF BONN

(ASSISTED BY DR. G. SCHROETER)

AUTHORIZED TRANSLATION

DI

EDGAR F. SMITH
PROFESSOR OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA

Third American from the Eighth German Edition

VOLUME II

CARBOCYCLIC AND HETEROCYCLIC SERIES

PHILADELPHIA

P. BLAKISTON'S SON & CO.

1012 WALNUT STREET

1902

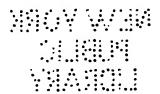


THE NEW YORK FUBLIC LIBRARY

306089

ASTOR, I ENOX AND TILDEN FOUNDATIONS. R 1904 L

Copyright, 1900, by P. Blakiston's Son & Co.



PREFACE

TO THE

THIRD AMERICAN EDITION.

In the preparation of the second volume of von Richter's organic chemistry Professor Anschütz availed himself of the services of all his colleagues who were especially interested in the experimental development of the chapters considered in the present text, so that the reader may rely upon its statements, which the translator has conscientiously striven to give a simple and correct English rendering.

The preparation of the index to this volume is due to the patient and painstaking efforts of Messrs. Walter T. Taggart, Owen L. Shinn, and J. Bird Moyer, to whom the translator would here acknowledge his deep obligations for the material aid thus given him in completing a work which has extended over a period of three years.

.

CONTENTS.

II. CARBOCYCLIC COMPOUNDS, 17.

Methods of Ring-formation in the case of the Cycloparaffins, 19.

I. TRI-, TETRA-, PENTA-, AND HEPTACARBOCYCLIC COM-POUNDS, 22.

- A. Trimethylene Group, 22. Trimethylene, 22. Trimethylene Carboxylic Acids, 22.
- Tetramethylene Group, 24.
- C. Pentacarbocyclic Compounds, 25. Pentamethylene, 25. Alcohols, 26. tones, 26. Adipinketone, 26. Carboxylic Acids, 27. Alcohol Carboxylic Acids, 27.
- D. Heptacarbocyclic Compounds, 28. Suberane, 28. Suberone, 28.

II. HEXACARBOCYCLIC COMPOUNDS, 29.

A. AROMATIC COMPOUNDS OR BENZENE DERIVATIVES CONTAINING A SINGLE NUCLEUS, 30.

The Benzene Derivatives, 30. Isomerism of the Benzene Derivatives, 32. Proof of the Equivalence of the Six Hydrogen Atoms in Benzene, 32. Basis of the Determination of Position of the Benzene Substitution Products, 34. Determination of the Positions in Diderivatives, 36. Isomerism of the Benzene Polysubstitution Products, 39. Constitution of the Benzene Nucleus, 39. Benzene Ring-formations, 41. Decompositions of the Benzene Ring, 44. I. Decomposition by Moderated Oxidation, 44. 2. Decomposition by Simultaneous Chlorination and Oxidation, 44.

- Decomposition by Reduction in Alkaline Solution, 47.

 I. Benzene Hydrocarbons Containing a Single Nucleus, 47.

 Coal Tar, 48. Alkyl Benzenes, 50. TOLUENE, 53. Cymene, 56.
- 2. Halogen Derivatives of the Benzene Hydrocarbons, 57.
- Nitrogen Derivatives of the Benzene Hydrocarbons, 63.
 Nitro-derivatives of Benzene and the Alkyl Benzenes, 64. Nitrobenzene, 66. Regularities in Substitution, 69.
 - 2. Nitroso-derivatives of Benzene and the Alkyl Benzenes, 69.
 - 3. \(\beta\)-Alphylhydroxylamines, 70.
 - 4. Nitroso- β -Alphylhydroxylamines, 70.
 - AMIDO-COMPOUNDS, or ANILINES, 70. A. PRIMARY PHENYLAMINES, 71.
 Aniline, 74. B. SECONDARY and TERTIARY PHENYLAMINES. Phenyl
 - ammonium Bases, 77. Alkylen-dianilines, 79. Alkylidene Anilines, 79. C. POLYPHENYLAMINES: Diphenylamine, 79. Triphenylamine, 80.

 Aniline Derivatives of Inorganic Acids: Aromatic Thionylamines, 80.

 Phosphorphenylamines, 80. Arsenphenylamines, 81.
 - Carbonic Acid Derivatives of the Primary and Secondary Amines, 81. Anilides of Monobasic Fatty Acids, 81. Formanilide, 82. Acetanilide,

Thioanilides, 83. Phenylated Amidines of Formic Acid and Acetic Acid, 83. Phenylated Carbylamines, 83. Phenylamine Derivatives of Oxy-acids, 84. Phenyl Glycocoll, 84. Homologous Anilido-fatty Acids, 84. Aniline Derivatives of Ketone Carboxylic Acids, 84. Aniline Derivatives of Carbonic Acid, 85. Carbanilic Acid, 85. Phenylated Ureas, 85. Carbanilide, 85. Phenylated Derivatives of the Thiocarbanic Acids and of Thiourea, 86. Phenylated Guanidine Derivatives, 88. Phenylated Nitriles and Imides of Carbonic Acid, 89. Phenylisocyanate, 89. Phenyl Mustard Oil, 89. Phenylated Cyanamide Derivatives, 90. Anilides of Dicarboxylic Acids, 90. Oxanilic Acid, 90. Oxanilide, 91. Phenylated Ure-Ides of Dicarboxylic Acids, 91. Aniline Substitution Products, 91. Aniline Haloids, 91. Nitranilines, 92. Nitrodiphenylamines, 93. Nitrosoderivatives of the Primary, Secondary, and Tertiary Aromatic Amines, 93. Nitrosodimethyl Aniline, 94. C. DIAMINES, 94. Phenylenediamines, 95. Condensations of o-Diamines, 95. Differences between the o-, m-, and p-Diamines, 96. Triamines, 97. Tetramines, 97. Pentamines, 97.

6. PHENYLNITROSAMINES, 97. 7. PHENYLNITRAMINES, 98. Diazobenzene Acid, 98. 8. DIAZO-COMPOUNDS, 99. 9. DIAZOAMIDO-COMPOUNDS, 106. 10. DISDIAZOAMIDO-COMPOUNDS, 106. DIAZO-AMIDO-BENZENE, 108. 11. DIAZO-OXYAMIDO-COMPOUNDS, 110. 12. DIAZOIMIDO-COMPOUNDS, IIO. Diazobensene Imide, III. 13. AZOXY-COMPOUNDS, III. Azoxy-benzene, III. 14. AZO-COMPOUNDS, II2. Azobenzene, II3. AMIDO-AZO-COMPOUNDS, II4. 15. HYDRAZINE COMPOUNDS, II6. Hydrazobenzene, 117. Benzidine and Semidine Rearrangement of Hydrazo-compounds, 117. Phenylhydrazine, 120. Phenylalkyl Hydrazines, 121. Phenylhydrazones, 122. Phenylhydrazine Derivatives of Inorganic Acids, Carboxylic Acid Derivatives of Phenylhydrazine, 125. Fatty Acid Derivatives, 125. Alcohol Acid Derivatives of Phenylhydrazine, 126. Phenylhydrazine Derivatives of the Mono ketonic Acids, 127. Phenylhydrazine Derivatives of Carbonic Acid, 127. Phenylhydrazine Derivatives of Dicarboxylic Acids, 129. Hydrazidines or Amidrazones, 129. Formazyl Compounds, 129. 16. PHENYLNITROSOHYDRAZINE, 131. 16 a. TETRAZONES, 131. 16 b. HYDROTETRAZONES, 131. 17. BUZYLENE OF DIAZOHYDRAZO-COMPOUNDS, 131.

4. Aromatic Compounds of Phosphorus, Arsenic, Antimony, Bismuth,

Boron, Silicon, and Tin, 131.

5. Phenyl Metal Derivatives, 133. Mercury-phenyl, 133.

6. Sulpho-acids, 133. CHLOR-, BROM-, IOD-, IODOSO-, NITRO-, NITROSO-, and AMIDOBENZENE SULPHONIC ACIDS, 136. Diazobenzene-sulphonic Acid Anhydrides, 137. Amido-azo-benzene-sulphonic Acids, 137. Phenylhydrazine Sulphonic Acids, 138. Sulphinic Acids, 138. Disulphoxides, 139. Sulphones,

139. Diphenylsulphone, 140.

7. Phenols. Monohydric Phenols, 140. Benzophenol, Phenol, Carbolic Acid, 142. Homologous Phenols, 144. Cresols, 143. Thymol, 144. Phenol Alcohol-ethers, 145. Anisol, 146. Phenol 146. Phenol Ethers, 146. Acid Esters of Phenol, 146. Phenol Substitution Products, 148. Phenol Haloids, 148. Nitrophenols, 149. Picric Acid, 150. Nitroso-compounds of Phenols, 155. Azophenols, 155. Oxyazobenzenes, 155. Sulphonic Acids of Phenol, 156. Thio-derivatives of Phenol, 156. Dinydric Phenols, 158. Pyrocatechin, 159. Resorcinol, 160. Orcinol, 162. Hydroquinone, 162. TRIHYDRIC PHENOLS; Pyrogallol, 164. Phloroglucin, 165. TETRAHYDRIC PHENOIS, 166. PENTAHYDRIC and HEXAHYDRIC PHENOIS, 166.

8. Quinones. Orthoquinones, 167. Paraquinones, 167. Quinone, 167. Quinone Haloids, Nitroquinone, 169. Amidoquinone, 170. Oxyquinones and Polyquinoyls, 170. Chloranilic Acid, 170. Quinone Nitrogen Derivatives, 172. Quinone Dioximes, Quinone-chlorimides, 172. Indophenols and Indo-

anilines, 173. Indamines, 174.

- 9. Phenyl-paraffin Alcohols and their Oxidation Products.
 - 1 a: Monohydric Phenyl-paraffin Alcohols and their Oxidation Products, 176.
 - 1. Monohydric Phenyl-paraffin Alcohols, 176. Benzyl Alcohol, 176. Bensyl Chloride, 177. Benzyl Sulphide, 178. Phenyl Nitro-paraffins: Phenylnitromethane, 178. Benzylamine, 179. Benzylhydroxylamines, 180. Substituted Benzyl Alcohols, 180.
 - 2. AROMATIC MONALDEHYDES, 182. Bensaldehyde, 183. 184. Derivatives of Benzaldehyde: Bensal Chloride, 184. Hydrobenzamide, 184. Benzaldoximes, 185. Substituted Benzaldehydes, 186.

3. AROMATIC MONO-KETONES, 188. Acetophenone, 189. Substituted

Acetophenones, 190.

Acetophenones, 190.
4. AROMATIC MONOCARBOXYLIC ACIDS, 191. Benzoic Acid, 193. Homologues of Benzoic Acid, 194. Alkyl Benzoic Acids, 194. Toluic Acids. 195. Cumic Acid, 195. Phenyl Fatty Acids, 196. Hydro-Acids, 195. Cumic Acid, 195. Phenyl l cinnamic Acid, 197. Hydratropic Acid, 197.

Derivatives of the Aromatic Monocarboxylic Acids, 197

- 1. Esters, 197. 2. AROMATIC ACID HALOIDS: Benzoyl Chloride, 198. 3. ACID ANHYDRIDES, 198. Benzoic Anhydride, 198. 4. ACID PER-OXIDES, 198. 5. THIOACIDS, 199. 6. ACID AMIDES, 199. Benzamide, 199. Hippuric Acid, 200. 7. ACID HYDRAZIDES, 200. 8. ACIDYLAZIDES, 201. 9. AROMATIC MONOCARBOXYLIC ACID NITRILES; 201. Benzonitrile, 202. Benzyl Cyanide, 203. 10. AMID-HALOIDS, 203. 11. Imide Chlorides, 203. 12. Phenylhydrazide Imide Chlorides, 203. 13. Imido-ethers, 203. 14. Thiamides, 204. 15. Imido-THIO-ETHERS, 204. 16. AMIDINES, 204. Benzamidine, 204. 17. DI-OXYTETRAZOTIC ACIDS, 205. 18. HYDRAZIDINES OF AMIDRAZONES, 205. 19. FORMAZYL DERIVATIVES, 206. 20. HYDROXAMIC ACIDS, 206. 21. HALOIDS OF BENZHYDROXIMIC ACID, 207. 22. AMIDOXIMES, 208. 23. Aromatic Nitrolic Acids, 208. 24. Ethyl Orthobenzoic Ester, 208. 25. BENZOTRICHLORIDE, 208. 26. ORTHOBENZOIC AMIDES, 209. Substituted Aromatic Monocarboxylic Acids, 209.
- 1. HALOGEN BENZOIC ACIDS, 209. 2. IODOSO- and IOD-BENZOIC ACIDS, 209. 3. NITROMONOCARBOXYLIC ACIDS, 210. 4. AMIDOMONO-CARBOXYLIC ACIDS, 211. Anthranilic Acid, 211. Isatoic Acid, 212. Oxindol, 214. Hydrocarbostyril, 214. 5. Diazobenzoic Acids, 215. 6. DIAZOAMIDOBENZOIC ACIDS, 215. 7. DIAZOIMIDOBENZOIC ACIDS, 215. 8. AZOXYBENZOIC ACIDS, 215. 9. AZOBENZOIC ACIDS, 215. 10. HYDRA-ZINE-BENZOIC ACIDS, 215. 11. SULPHOBENZOIC ACIDS: Saccharin, 216. 1 b. Monohydric Oxyphenyl-paraffin Alcohols and their Oxidation
 - Products, 217. I. MONOHYDRIC OXYPHENYL-PARAFFIN ALCOHOLS, OR PHENOL ALCO-
 - HOLS, 217. Saligenin, 217. 2. AROMATIC OXYMON-ALDEHYDES, PHENOL ALDEHYDES, 218. Salicylic Aldehyde, 218. Anisic Aldehyde, 219. Protocatechnic Aldehyde, Vanillin, 219. Piperonal, 220.

3. PHENOL KETONES, 220.

- 4. PHENOL MONOCARBOXYLIC ACIDS, 221. Salicylic Acid, 222.
 Anisic Acid, 225. Protocatechuic Acid, 227. Gentisinic Acid, 229.
 Orsellic Acid, 229. Gallic Acid, 230. Tannic Acids, 231.
 2. Polyhydric Aromatic Alcohols, in Which Only One Hydroxyl is
- Present in Each Side-chain, and their Oxidation Products, 232.
 - I. DI- AND TRIHYDRIC AROMATIC ALCOHOLS: Xylylene Alcohols, 232. 2. ALDEHYDE ALCOHOLS, 233.
 - AROMATIC DIALDEHYDES, 233.
 - 3. Aromatic Dialdehydes, a 4. Di- and Triketones, 233.

 - 5. ALCOHOL CARBOXYLIC ACIDS, 233. Phthalide, 234. Meconine, 235. 6. ALDEHYDE ACIDS, 236. Phthalaldehydic Acid, 236. Opianic Acid, 237.

CONTENTS.

7. KETONE CARBOXYLIC ACIDS, 238.

8. DICARBOXYLIC ACIDS, 239. Phthalic Acid, 239. Isophthalic Acid, 242. Terephthalic Acid, 243. Aromatic Dicarboxylic Acids Uvitic Acid, 242. Containing 1 CO, H in the Nucleus and One in the Side-chain, 244. Aromatic Dicarboxylic Acids Having the Carboxyls in Different Side-groups,

9. ALDEHYDO-CARBOXYLIC ACIDS, 245.

10. TRICARBOXYLIC ACIDS, 245. Trimesic Acid, 245.

11. TETRACARBOXYLIC ACIDS, 246.

12. PENTACARBOXYLIC ACID, 246.

Mellitic Acid, 246. 13. HEXACARBOXYLIC ACID, 246.

3. Aromatic Polyalcohols, Containing More Than One Hydroxyl Group in the Same Side-chain, and Their Oxidation Products, 247.

1. Phenyl Glycols and Phenyl Glycerol, 247. Stycerine, 248.

2. PHENYLALCOHOL ALDEHYDES: Phenyltetrose, 248. 3. PHENYL KETOLS, 248. Acetophenone Alcohol, 248.

4. PHENYL ALDEHYDE KETONES, 249. Phenyl Glyoxal, 249.

5. PHENYL PARAFFIN DIKETONES: Benzoyl Acetyl, 250. Acetyl Acetophe-

none, 250. Acetophenone Acetone, 250.

6. PHENYL PARRAFFIN ALCOHOL ACIDS: A. Monoxyalcohol Acids: Mandelic Acid, 251. Phenyl-lactic Acids: Atrolactinic Acid, 252. Tropic Acid, 252. Phenylalanine, 253. Tyrosine, 253. B. Dioxyalcohol Acids: Atroglyceric Acid, 255. Styceric Acid, 255. C. Trioxyalcohol Acids, 256.

7. PHENYLPARAFFIN-ALDRHYDE CARBOXYLIC ACIDS, 256.

8. PHENYLPARAFFIN-KETONE CARBOXYLIC ACIDS: A. a-Ketone-carboxylic Acids, 257. Phenylglyoxylic Acid, 257. Isatin, 258. B. Phenylparaffin β -ketone Carboxylic Acids, 259. Benzoyl Acetic Acid, 259. C. γ - and d-ketone Carboxylic Acids, 261.

9. PHENYL-ALCOHOL-KETONE CARBOXYLIC ACIDS, 261.

- 10. PHENYL DIKETONE CARBOXYLIC ACIDS: Quinisatinic Acid, 261. Benzoyl Pyroracemic Acid, 261. 11. PHENYLPARAFFIN DICARBOXYLIC ACIDS, 262. Phenylmalonic Acid,
- 262.
- 12. PHENYL-ALCOHOL DICARBOXYLIC ACIDS, 262. Phenylmalic Acids, 263. 13. PHENYLKETONE DICARBOXYLIC ACIDS: Benzoyl Malonic Ester, 263.
- 14. PHENYL-OXYKETONE DICARBOXYLIC ACIDS, 264.
- 15. PHENYLPARAFFIN TRICARBOXYLIC ACIDS, 264.

16. PHENYLKETO-TRICARBOXYLIC ACIDS, 264.

- PHENYLENE OXYDICARBOXYLIC ACIDS, 264. Phthalid-acetic Acid, 264.
 PHENYLENE KETONE DICARBOXYLIC ACIDS, 265. Phthalonic Acid, 265.

19. TRI- and TETRA-CARBOXYLIC ACIDS, 265.

20. OXYTRI- and PENTACARBOXYLIC ACIDS, 265.

21. KETONE TRICARBOXYLIC ACIDS, 266.

Mono-nucleus, Aromatic Substances with Unsaturated Side-chains, 266.

1a. OLEFINE BENZENES: Styrolene, 266. 1b. Acetylene Benzenes: Phenyl-

acetylene, 268. Ic. DIOLEFINE BENZENES.

- 2a. OLEFINE PHENOLS: A. Olefine Monoxybenzenes, 269. Chavicol, 269. B. Olefine Dioxybenzenes, 269. Eugenol, 270. Safrol, 270. C. Olefine Trioxybenzenes, 270. D. Olefine Tetraoxybenzenes, 271. Apiol, 271. 2b. Acetylene Phenetol, 271.
- 3. PHENYLOLEFINE ALCOHOLS WITH THEIR OXIDATION PRODUCTS. Phenylolefine Alcohols, 271. Styrene, 271. 1b. Oxyphenylolefine Alcohols: Coniferyl Alcohol, 272. 2a. Phenylolefine Aldehydes: Cinnamic Aldehyde, 272. 2b. Oxyphenylolefine Aldehydes, 272. 3. Phenyldi-

olefine Aldehydes, 272.

48. PHENYLOLEFINE KETONES: Benzal Acetone, 272.

49. Oxyphenylolefine Ketones, 273.

5. Phenyldiolefine Ketones, 273.

6. Phenyldiolefine Ketones, 273.

6. Phenyldiolefine Ketones, 273.

6. Cinnamic olefine Carboxylic Acids, 273. Vinyl Benzoic Acid, 273.

Acid, 274. Cinnamic Acids Substituted in the Benzene Nucleus, 276. Homologous Cinnamic Acids, 278. Atropic Acid, 278. 7. Oxyphenyl-olefine Carboxylic Acids, 279. A. Monoxyphenyl-olefine Carboxylic Acids, 279. A. Monoxyphenyl-olefine Carboxylic Acids, 282. Caffele Acid, 282. Umbelliferone, 283. C. Trioxycinnamic Acids, 283. D. Tetra-oxycinnamic Acids, 283. 8. Phenylacetylene Carboxylic Acids, 283. D. Tetra-oxycinnamic Acids, 283. 8. Phenylacetylene Carboxylic Acids, 284. Phenyl-propiolic Acid, 284. 9. Phenyldiolefine Carboxylic Acids, 285. Piperic Acid, 285.

4. Compounds which may be Viewed as Oxidation Products of Mononucleus, Aromatic Polyalcohols with Unsaturated Side-chains, 285. 1. Phenylene Oxyolefine Carboxylic Acids, 285. Isocoumarin, 286. Isocarbostyril, 286. 2. Phenylene Aldehydo-carboxylic Acids, 286. 3. Phenylene Dicarboxylic Acids, 286. 4. Phenylolefine Ketols, 287. 5 and 6. Phenyl-oxyolefine and Diolefine Carboxylic Acids, 287. 7 and 8. Phenyl-olefine and Diolefine-a-keto-carboxylic Acids, 287. 9. Phenylolefine-β-ketone Carboxylic Acids, 287. 10. Phenyl-olefine-γ-ketone Carboxylic Acids, 288. Benzal-lævulinic Acid, 288. 11 and 12. Phenylolefine and Diolefine Carboxylic Acids, 288. Benzal Malonic Acid, 288. Phenyl Maleic Acid, 289. Cinnamenyl Malonic Acid, 289. 13. Phenylene Oxyolefine Dicarboxylic Acids, 289. Phthalyl Acetic Acid, 289. 14. Phenylene Oxyolefine Tricarboxylic Acids, 290.

B. HYDROAROMATIC SUBSTANCES WITH SINGLE NUCLEUS, HYDROBEN-ZENE DERIVATIVES, 290.

- 1. Hydroaromatic Hydrocarbons, 290. 1a. Hexahydrobenzenes, Naphthenes, 291. Hexahydrobenzene, 292. Halogen Substitution Products of the Hexahydrobenzenes, 292. Benzene Hexachloride, 293. Ib. Tetrahydrobenzenes, Naphthylenes: Tetrahydrobenzene, 293. Ic. Dihydrobenzenes: Dihydrobenzene, 294.
- 2. Ring-alcohols of the Hydroaromatic Hydrocarbons: Quinite, 294. Quercite, 295. Inosite, 295.
- 3. Ring-amines of the Hydroaromatic Hydrocarbons, 295.
- 4. Ring-ketones of the Hydroaromatic Hydrocarbons, 296. a. Ring-ketone of Hexamethylene: Pimelin Ketone, 296. Dihydroresorcinol, 296. b. Ring-ketones of the Tetrahydrobenzenes, 298. c. Ring-ketones of the Dihydrobenzenes, 299.
- Hydroaromatic Carboxylic Acids, 299.
 Hydroaromatic Monocarboxylic Acids: A. Hexahydrobenzoic Acids, 300.
 Hexahydro-oxybenzoic Acids, 301. Quinic Acid, 301. C. Ketohydromonocarboxylic Acids, 301. 2. Hydroaromatic Dicarboxylic Acids: Hydrophthalic Acids, 302. Oxy- and Ketohydrobenzene Dicarboxylic Acids, 304. Succino-succinic Acid, 305. 3. Hydrobenzene Tricarboxylic Acids, 306. 4. Hydrobenzene tetracarboxylic Acids, 5. Hexahydrobenzene-hexacarboxylic Acids, 307.

TERPENES, 307.

- A. Olefinic Terpene Group, 309. I. Olefinic Terpenes, 309. 2. Olefinic Terpene Alcohols, 309. 3. Olefinic Terpene Aldehydes, 310. Citronellal, Citral, 310. 4. Olefinic Terpenic Acids, 310.
 B. Terpan or Menthan Group. 1. HYDROCARBONS: Limonene and
- Dipentene Group, 310. Terpinene and Phellandrene, 312. Hydroterpenes, 313.
 - 2. Alcohols of the Terpan or Menthan Group: Menthol, 313. pine, 314. Cineol, 315. Terpineols, 316.
 3. Bases of the Terpan or Menthan Group, 317.
 - 4. RING-KETONES of the Terpan or Menthan Group: Menthone, 318. Carvone, 320.
- C. Camphan Group, 321. 1. Hydrocarbons: Camphene, 321. Pinene, 322. Decomposition Products of Pinene, 323. Terebic Acid, 324. Ter-

penylic Acid, 324. 2. Alcohols: Borneol, 324. 3. Amines, 326. 4. Ketones: Camphor, 327. Constitution of Camphor, 327. Transposition Products of Camphor, 328. Camphoric Acid, 331. Fenchones, 333. RESINS, 334.

AROMATIC HYDROCARBONS CONTAINING SEVERAL NUCLEI, 335.

A. Phenylbenzenes and Polyphenyl-fatty Hydrocarbons, 335.

I. Phenylbenzene Group: Diphenyl, 335. Benzidine, 337.

Diphenic Acid, 340. Diphenylbenzenes, 341. Triphenyl Benzenes, 342.

II. BENZYLBENZENE GROUP: Diphenyl Methane, 342. Benzhydrol, 344. Benzophenone, 345. Auramine, 348. Oxybenzophenones, 348. Carboxylic Acids: Benzyl-benzoic Acid, 349. Benzhydrylbenzoic Acid, 349. Benzophenone-carboxylic Acid,

349. Benzyl Diphenyls, 350. Dibenzyl Benzene, 350.

III. TRIPHENYL METHANE GROUP: Triphenyl Methane, 351.

Tetramethyldiamidotriphenyl Methane, 352. Triphenyl Cart binol, 353. Malachite Green, 354. Rosaniline, 355. Methyl Violet, 358. Phenylated Rosanilines, 359. Phenol Derivatives: Leucaurine, 360. Benzelnes, 360. Rosamines, 360. Aurine, 361. Rosolic Acid, 361. Eupittonic Acid, 361. Carboxyl Derivatives, 361. Benzene Phthalin, 361. Diphenylphthalide, 362. Phthaleins, 363. Fluorescein, 365. Rhodamines, 366.

IV. DIPHENYL ETHANE GROUP, 367. A. Un-Diphenyl Ethane Derivatives, 367. Benzilic Acid, 369. Triphenyl Acetic Acid, 369. B. Sym. Diphenyl Ethane Group, 369. Dibenzyl, 369. Stilbene, 370. Tolane, 371. I. Alcohol and Ketone Derivatives of Dibenzyl, 371. Desoxybenzoin, 371. Hydrobenzoins, 371. Benzoin, 372. Benzil, 373. 2. Alcohol Derivatives of Stilbene, 375. Isobensil, 375. Haloid Stilbene, 375. Page 2015. Stilbenes, 375. Carboxylic Acids of the Dibenzyl Group, 375. Tri and Tetra-phenyl Ethane Group, 377. Benzpinacone, 378.

V. DIPHENYL PROPANE GROUP, 378. Dibenzyl Ketone, 378. Dypnone, 379. Carboxylic Acids, 379.

VI. DIPHENYL BUTANE GROUP, 380. Diphenyl Diacetylene, 380. Diphenacyl, 380. Bidesyl, 381. Diphenyl Tetraketone, 381. Carboxylic Acids, 381. Vulpic Acid, 382.
VII. DIPHENYLPENTANE GROUP, 383. Benzamarone, 383.

VIII. DIPHENYL HEXANE GROUP and higher homologues, 383. Oxalyldiacetophenone, 383.

B. Condensed Nuclei, 384.

1. Indene and Hydrindene Group, 384. Indene, 384. Hydrindene,

387. Hydrindone, 387. Diketohydrindene, 388.

2. NAPHTHALENE GROUP, 389. Constitution of the Naphthalene Nucleus, 389. Isomerisms of Naphthalene Derivatives, 390. Naphthalene thalene Ring formations, 390. Decompositions of the Naphthalene

Ring, 392. Naphthalene, 394. Naphthalene Homologues, 394. I. Haloid Naphthalenes, 395. 2. Nitronaphthalenes, 395. Nitrosonaphthalenes, 396. 4. Naphthylamines, 396. 5. Diazo and Azo-compounds of Naphthalene, 397. Naphthalene Red, 398. 6. Naphthyl Hydrazines, 398. 7. Sulphonic Acids, 398. Naphthylamine Sulphonic Acids, 399. Naphthionic Acid, 399. Congo Red, 399. Rocellin, 400. Naphthol Black, 400. 8. Naphthalene Sulphinic Acids, 400. 9. Naphthols, 400. Nitronaphthols, 401. Martius Yellow, 401. Amido-naphthols, 401. Azo-naphthols, 401. Bieberich Scarlet, 402. Naphthol Orange, 402. Naphthol Sulphonic

Acids, 402. Amido-naphthol Sulphonic Acids, 403. Dioxynaphthalenes, 403. Trioxynaphthalenes, 404. Thionaphthols, 404. Io. Quinones, 404. Juglone, 405. Nitrogen Derivatives of the Naphthoquinones, 406. Nitrosonaphthols, 406. Naphthoquinone Dioxime,

406. Naphthoquinone Chlorimide, 407. Anils, 407.

11. Alcohols of the Naphthalene Series and their Oxidation Products, 407. Naphthobenzyl Alcohol, 407. Naphthaldekyde, 407. Naphthyl Methyl Ketone, 407. Naphthoic Acids, 408. Naphthol Carboxylic Acids, 408. Naphthalic Acid, 409. Naphthonitriles, 409. Cyan-naphthalenes, 409. 12. Dinaphthyls, 409. Dinaphthyl

Methanes, 409. 13. Acenaphthene, 410. 14. Hydronaphthalene Derivatives, 410. A. Dihydronaphthalenes, 411. B. Tetrahydronaphthalenes, 411. ac- and ar- Tetrahydronaphthylamines and Naphthols, 412. C. Hexa-, Octo-, Deca-, and

Dodeca hydronaphthalenes, 413.
3. PHENANTHRENE GROUP, 413. Phenanthraquinone, 415. Retene, 415.

 Chrysene, 416. Picene, 416.
 Fluorene Group, 417. Retene-, Chrysene-, Picene-fluorene, 417. Bifuorene, 418. Diphenylene Ketone, 419. Fluorenone, 419. Carboxylic Acids, 419. Fluoranthene, 420. Pyrene, 420.
 Anthracene Group, 420. Anthracene, 422. Alkylic Anthracenes, 422. Substituted Anthracenes, 423. Oxyanthracenes, 423. Anthrol, 423. Anthranol, 424. Hydroanthracenes, 424. Hydro-anthranol and Oxanthranol, 425. Anthraquinone, 425. Anthraquinone Sulphonic Acids, 426. Oxyanthraquinones, 426. Alisarin, 427. Alisarin, 427. arin Orange, 427. Purpurin, 428. Anthraquinone Carboxylic Acids,

429. Naphanthraquinone, 429.

GLYCOSIDES and PENTOSIDES, 429. Myronic Acid, 429. Arbutin, 429.

Salicin, 430. Anygdalin, 430. Coniferine, 430. Phloridzin, 430. Iridin, 431. Digitalin, 431.
PENTOSIDES, RHAMNOSIDES, 431. Naringin, 432. Hesperidin, 432. Quercitrin, 432. Frangulin, 432.

BITTER PRINCIPLES, 432. Cantharidin, 432. Picrotoxin, 432. Santonin, 432.

NATURAL DYES, 433. Brasilin, 433. Hamatoxylin, 433. Curcumin, 433. Carminic Acid, 433. Chlorophyl, 434.

III. HETEROCYCLIC COMPOUNDS, 435.

Homologous Series, 437.

1. THREE-MEMBERED HETEROCYCLIC COMPOUNDS, 444.

A. Monoheteroatomic Three-membered Rings, 444. Ethylene Oxide, 444. Tolane Sulphide, 444. Lactimides, 444. B. Diheteroatomic Three-membered Rings, 444. Hydrazi- and Azimethylene Group, 445. Diazomethane, 445.

2. FOUR-MEMBERED HETEROCYCLIC SUBSTANCES, 446.

A. Monoheteroatomic Four-membered Rings, 446. B. Diheteroatomic Fourmembered Rings, 446. Betaines, 446.

3. FIVE-MEMBERED HETEROCYCLIC SUBSTANCES, 447.

A. Monoheteroatomic Five-membered Rings, 447.

FURFURANE GROUP, 448. Furfurane, 448. Furfurol, 449. Pyromucic Acid, 450. Uvinic Acid, 451. Hydrofurfuranes, 451.
 THIOPHENE GROUP, 452. Thiophene, 452. Thiophene Homologues, 453.

Haloid Thiophenes, 454. Nitrothiophenes, 454. Thiophenin, 455. Thiophene Carboxylic Acids, 455. Thiophthene, 456.

3. Selenophene, 456.

 PYRROL GROUP, 456. Pyrrol, 456. n-Derivatives of Pyrrol, 458. c-Alkyl Pyrrols, 458. Haloid Pyrrols, 459. Iodol, 459. Nitropyrrols, 459. Pyrrol-azo-compounds, 459. Pyrrol Ketones, 460. Pyrrol Carboxylic Acids, 460. Pyrocoll, 460. Hydropyrrol Derivatives: Pyrroline, 461. Pyrrolidine, 461.

CONDENSED NUCLEI OF THE FURFURANE, THIOPHENE, AND PYRROL GROUPS,

5. Benzofurfurane or Coumarone Group, 463. COUMARONE, 464. Coumarilic Acid, 464. Benzodi- and trifurfuranes, 464.

6. BENZOTHIOPHENE GROUP, 465. Thionaphthene, 465.
7. BENZPYRROL or INDOL GROUP, 465. Indol, 465. Homologous Indols, 466. Skatole, 467. Indol Sulphonic Acids, 468. Indo Carboxylic Acids, 468. Oxindol Derivatives, 468. Indoxyl, 468. Indoxylic Acid, 469. Indogenides, 469. HydroIndol Derivatives, 470. Dihydromethyl Ketol, 470. Indolinons, 470. Oxindol, 471. Dioxindol, 471. Isatin, 471. Isatin Chloride, 472. Indigo Blue, 473.—History, 473. Syntheses, 473.—Constitution, 475. Derivatives, 475. Indigo White, 476.

8. DIBENZOFURFURANE, DIPHENYLENE OXIDE, 476.

9. DIBENZOFYRROL, CARBAZOLE, 477. Hydrocarbazoles, 477.

Naphthophenocarbazole, 478. Dinaphtho-carbazole, 478.

B. Polyheteroatomic Five-membered Rings, 478. Nomenclature of Azoles,

478. Arrangement of Azoles, 479.

I. Pyrazole Group, 480. Pyrazole or Pyrro-[a]-monazole, 481. Homologous Pyrazoles, 481. Haloid-, nitro-, amidopyrazoles, 483. Pyrazole Sulphonic Acids, 483. Oxypyrazoles, 483. Pyrazoles, 484. Pyrazole Carboxylic Acids, 484. Pyrazolines, 485. Pyrazolons, 486. Pyrazolon, 487. Antipyrine, 488. Pyrazolon Carboxylic Acids, 489. Pyrazolidines, 490. Pyrazolidines, 490. Pyrazolidones, 490. Indazolos or Benzo pyrazolos, 493.

3. ISOXAZOLE GROUP, 493. Isoxazole or furo-[a]-monazoles, 493. Isoxazolons, 495.

4. Indoxazene of Benzisoxazole Group, 495. Phenyl Indoxazene,

5. GLYOXALINES OF IMIDAZULES, 496. Glyoxaline, 497. Lophine, 498. Hydroglyoxalines, 498. Lysidine, 499. Amarine, 499. Imidazolons, 499. Keto-, thio-, diketo-, imidoketotetrahydroglyoxalines, 499.

6. BENZOGLYOXALINES OF BENZIMIDAZOLES, 499. Benzimidazole, 500. Methyltolimidazole, 501. Keto-, Thio-, and Imido-benzimidazolines, 502. Phenylene Urea, 502. Phenylene Sulpho-urea, 502.

7. Oxazoles or Furo-[b]-monazoles, 502. Oxazolines, 503. Alkylene-Yureas, 503.

8. Benzoxazoles, 503. Benzoxazole or Methenylamidophenol, 504. Oxy-, Thio-, and Amido-benzoxazoles, 504.

9. THIAZOLES or Thio-[b]-mon reoles, 504. Amido-thiazole, 505. Oxythiazoles, 505. Thiazole Carboxylic Acids, 506. Sulphwinic Acid, 506. Thiazolines, 506. Alkylen-Y-thioureas, 507. Mustard Oil Acetic Acid, 507.

 BENZOTHIAZOLES, 507. Benzothiazole or Methenyl-amidothiophenol, 507. Dehydrothiotoluidine, 507. Thioflavin, 508. Primulin, 508. Chlorphenyl Mustard Oil, 508.

SELENAZOLES, 508. Trimethylene Selenurea, 508.

 OSOTRIAZOLES or Pyrro-[aa₁]-diazoles, 508. Osotriazole Carboxylic Acids, 509. Pseudo azimidobenzenes or benzosotriazoles, 509. Azammonium Hydroxides, 510.

Benzopyrro[ab]diazoles, 510. 12. Pyrro-[ab]-diazoles, 510.

Benzenes, 510. Azimidazoles, 511.

13. TRIAZOLES or Pyrro [ab₁]-diazoles, 511. Triazolons, 513. Urazoles, 514. Guanazoles, 514.

- 14. FURAZANES, Asoxazoles or Furo[aa,] diasoles, 514. Benzo-, Naphtho-, and Phenanthro-furazanes, 515.
- 15. AZOXIMES of Furo[ah] diasoles, 515. Ethenyl Benzenyl Azoxime, 515.
- 16. OXYBIAZOLES or Furo[bb,] diasoles, 516. Keto-, Thio-, and Imidooxybiazolines, 516.

- 17. DIAZO-OXIDES or Benso- and Naphtho-furo ab diazoles, 516.
 18. AZOSULPHIMES or Thio ab diazoles, 517. Dibenzyl Azosulphime, 517.
 19. THIO b diazoles, 517. Thiobiazolines, 517. Keto- and imidothiobiazolines, 517.
- 20. THIO[ab]DIAZOLES, 518. Phenylene Diazosulphides or benzothio[ab]diazoles, 518.
- 21. PIAZTHIOLES and PIASELENOLS or Benzothio [aa,] diazoles and Benzoseleno-[a₁a₁] diazoles, 518.

 22. Thio[abb₁] TRIAZOLES or TRIAZSULPHOLES, 518.

23. TETRAZOLES or Pyrrotriasoles, 519. Benzenyl Tetrazotic Acid, 520. Amidotetrazotic Acid, 520. Diazotetrazole, 520. Tetrazolium Compounds, 520.

4. SIX-MEMBERED HETEROCYCLIC COMPOUNDS, 521.

A. Monoheteroatomic Six-membered Rings, 521.

1. Six membered Rings with an O-member, 521. a-Pyrone, Coumalin, 522. Isodehydracetic Acid, 522. \(\gamma\)-Pyrones, 522. Meconic Acid, 523. Benzoa-pyrones: Coumarins and Isocoumarins, 523. Benzo-\(\gamma\)-pyrones: Chrysin,
Fisetin, Quercetin, 523. Dibenzo-pyrones or Xanthones, 524. Xanthone, 524. Euxanthone, 525. GentiseIn, 525. Pyronine, 525.

2. Six-membered Rings Containing one S-member, 525. Penthiophene, 525.

Thioxanthene, 526. Thioxanthone, 526.

3. Six-membered Rings Containing an N-member, 526. I. PYRIDINE GROUP, 526. Constitution of Pyridine, 527. Synthesis of the Pyridines, 528. Behavior of Pyridine Bases, 530. Isomerisms, 531. Pyridine, 531. Homologous Pyridines, 532. Halogen Pyridines, 533. Pyridine Sulphonic Acids, 533. Nitro- and amido-pyridines, 533. Oxypyridines, 533. a-Pyridine, 534. Pseudoluidostyril, 534. y-Pyridone, 534. y-Lutidone, 534. Dioxypyridines, 534. Glutaconimide, 534. Trioxypyridines, 535. Glutasine, 535. Pyridyl Alkines, 535. Pyridyl Ketones, 535. Pyridine Monocarboxylic Acids. Picolinic Acid, Nicotinic Acid, Isonicotinic Acid, 536. Pyridine Dicarboxylic Acids: Quinolinic Acid, Isonicotinic Acid, 530. Pyridine Dicarboxylic Acids: Quinolinic Acid, Cinchomeronic Acid, 536. Pyridine Tri-, Tetra-, and Penta-carboxylic Acids, 537. Oxypyridine Carboxylic Acids, 537. Phenyl-lutidone Carboxylic Acid, 538. Comenanic Acid, 538. Citrazinic Acid, 538. Pyridyl Substituted Acids of the Fatty Series: Pyridyl Lactic Acids, Pyridyl Acrylic Acid, 538. Hydropyridine Derivatives, 538. Piperidine, 538. Decomposition of the Piperidine Ring, 539. Piperidine Carboxylic Acid, 540. Eucaine, 540.

II. QUINOLINE GROUP, 541. Syntheses of Quinoline Derivatives, 542. Behavior of the Quinolines, 544. *Quinoline*, 545. Homologous Quinolines, 545. *Quinaldine*, 546. Haloid, Sulpho-, and Nitro-derivatives of the Quinolines, 547. Amidoquinolines, 547. Oxyquinolines, 547. Analgen, 547. Carbostyril, 548. Lepidone, 548. Kynurine, 549. Quinoline Aldehydes and Ketones, 549. Quinoline Carboxylic Acids, 549. Cinchoninic Acid, 549. Oxyquinoline Carboxylic Acids, 550. Xanthoquinic Acid, 550. Quinic Acid, 550. Hydroquinolines, 550. Tetrahydroquinoline, 551. Decahydroquinoline, 551. Julole and Lilole

Derivatives, 552.

III. CONDENSED Quinolines, 552. Naphthoquinoline, 553. Alizarin Blue, 554. Anthraquinoline, 554. Phenanthroline, 554. Quinoquinolines, 554.

IV. Isoquinoline Group, 554. Isoquinoline, 555. Homologous Isoquinolines, 556. Oxyisoquinolines, 556. Isocarbostyril, 556. Hydroisoquinolines, 557. Tetrahydroisoquinoline, 557. Hydroisocarbostyril,

V. PHENANTHRIDINE, 557. Phenanthridone, 558. VI. NAPHTHYRIDINE and NAPHTHINOLINE, 558.

VII. ACRIDINE GROUP, 559. Acridine, 560. Chrysaniline, 560. Acridone, 560. Carbazacridine, 561. Quinacridine, 561.

VIII. Anthrapyridines, 561.

Alkaloids, 561.

I. Pyridine Group of the Alkaloids, 562. *Piperine*, 562. Conine, 562. Decomposition and Synthesis of Conine, 563. Trigonelline,

565. Arecaldine, 565. Pilocarpine, 565. Nicotine, 565.

II. TROPINE GROUP, 567. Solanum Bases, 567. Atropine, 567.

Tropelnes, 567. Tropine, 568. Decomposition and Synthesis of Tropine, 568, 569. Cocaine, 569. Truxillic Acids, 569. Tropa-cocaine, 569. Ecgonine, 570. Anhydroecgonine, 570. Pelletierine, 571. Methyl Granatoline, 571.

III. Quinoline Group of the Alkaloids, 571. Quinine, 571. Cinchonine, 572. Decomposition and Oxidation of Cinchonine and Quinine, 572, 573. Decomposition of Apocinchene, 574. Synthesis of y,o-Oxyphenylquinoline, 574. Strychnos Bases, 575. Strychnine, 575.

Brucine, 575. Veratrine, 575.

IV. ISOQUINOLINE GROUP OF THE ALKALOIDS, 575. Opium Bases, 575. Morphine, 576. Papaverine, 576. Narcotine, 577. Hydrastine, 578. Berberine, 579.

B. Polyhetero-atomic Six-membered Rings: AZINES, 579. Nomenclature, 579. 1. A. Oxazines, 580. Benzorthoxazinon or o-Benzaldoxime and o-Benzoke-

toxime Carboxylic Anhydrides, 580.

B. METOXAZINES: Pentoxazolines, 580. Benzometoxazines or Phenpentoxazolines, 580. Coumazonic Acids, 580. Imido and Thiocoumazones, 581.

C. PAROXAZINES: Morpholines, 581. Benzoparoxazines, 581. Dibenzoparoxazines or Phenoxazines, 581. Phenoxazine Dyes: Resorufin,

Gallocyanine, 582.

- 2. THIAZINES: A. Orthothiazines, 582. B. Metathiazines, 582. Penthiazolines, 583. Benzometathiazines or Phenpenthiazolines, 583. Imidoand Thio-coumothiazones, 583. C. Parathiasines: Dibensoparathiasine, 583. Thiodiphenylamine, 583. Thionine Dyes, 584. Methylene Blue, 584.
- DIAZINES: A. Orthodiazines, 584. Pyridazine, 584. Dihydropyridazines, 585. Pyridazinones, 585. Orthopiperazones, 586. Benzorthodiazines: Cinnoline and Phthalasine, 586. Dibenzorthodiazines: Phenazone, 587. Cinnoline and Phthalasine, 586. Dibenzorthodiazines: Phenazone, 587. B. Metadiazines: Pyrimidines, 587. Cyanalkines, 588. Hydropyrimidines, 588. Uracil Derivatives, 589. Benzometadiazines: Quinazolines or Phenmiasines, 589. Hydro- and Ketohydroquinazolines, 589, 590, 591. C. Paradiazines: Pyrazines or Piazines, 592. Piperazines, 594. Benzoparadiazines: Quinoxalines, 594. Dibenzoparadiazines: Phenazine Group, 597. Amido-phenazines or Eurhodines, 599. Diamidophenazines, 599. Toluylene Red, 599. Oxyphenazines or Eurhodols, 600. Azonium Compounds, 600. Indulines, Indones, and Safranines, 600. Benzoindulines, 601. Rosindulines, Isomesindulines, 601. Naphthindulines, 601. dulines, 601. Rosindulines, Isorosindulines, 601. Naphthindulines, 601. Safranines, 602. Fluorindenes, 603.

4. TRIAZINES: A. Cyanidines, 604. Cyanphenine, 604. B. Unsym. (a)-Triazines, 605. Phen-a-triazines, 605. Phendihydro-a-triazines, 606.

C. a- or β -triazines: Phendihydro- β -triazines, 606. 5. TETRAZINES: A. Osotetrazones, 606. Phendihydrotetrazine, 606. Iso-

phendihydrotetrazines, 606. Urazine, 607.

6. Substances Consisting of Polyhetero-atomic Six-membered Rings, which Contain O- and S-members, in Addition to Nitrogen, 607. Benzenylamidoxime-acetic Acid Isoanhydride, 608. Azoxazine Derivatives, 608. Diazthines, 608. Thialdines, 608.

A TEXT-BOOK

OF

ORGANIC CHEMISTRY.

II. CARBOCYCLIC COMPOUNDS.

(Compounds containing carbon rings.)

The derivatives of methane considered in the first volume consist of open carbon chains. Following these are those derivatives which have closed carbon chains or carbon rings. They are called carbocyclic compounds. In contrast to them are the azocyclic derivatives, which contain a ring consisting entirely of nitrogen atoms: e.g., hydrazoic acid and its derivatives. The carbocyclic compounds are usually called isocyclic derivatives. This latter designation is, however, too comprehensive, as it includes bodies containing a ring composed of atoms of any one element at pleasure. In contradistinction to the isocyclic derivatives there are also the heterocyclic derivatives. In the latter, atoms of different elements have taken part in the formation of the ring (1, 78).

The carbocyclic hydrocarbons are the ring-shaped hydrocarbons, consisting of from three to seven methylene groups, which are isomeric with the olefines of like carbon content. They are either called polymethylenes, from the number of methylene groups present in them, or they are named after their isomeric olefines, to which is added the prefix R—i. e., R-olefines (B. 21, 2720 Anm.; 26, 1085 Anm.); or, in accordance with the decision of the Geneva Conference, they take the name of the normal hydrocarbons with like carbon content, and add to the same the prefix "cyclo"—e. g., cycloparaffins. The first and third designations are preferred.

Hexamethylene is also called hexahydrobenzene, and heptamethylene is known as suberane.

Consult B. 29, 587, for the nomenclature of ring-shaped bodies.

Olefines and diolefines followed the normal hydrocarbons. In the same manner we find cyclo-olefines, cyclodiolefines, and cyclotriolefines attaching

themselves to the cycloparaffins.

Benzene, of all the carbocyclic forms, demands especial consideration. It is the parent hydrocarbon of the aromatic or benzene derivatives, the most numerous of the compounds of carbon. Accepting, with Aug. Kekulé, the presence in benzene of a ring of six carbon atoms joined by an alternate single and double union to one another, then benzene would be a cyclotriolefine:

The addition of hydrogen converts benzene into hexahydrobenzene, hexamethylene, or cyclohexane. The transformation products of aromatic derivatives, which can be referred to dihydro- or tetrahydrobenzene—[cyclohexadiën] and [cyclohexene]—as the parent substances, are constantly growing in number. It has become customary to consider them, in conjunction with the hexamethylene or hexahydrobenzene com-

pounds, as hydroaromatic derivatives.

Many naturally occurring bodies, particularly the terpenes and camphor, belong in this group. By rigid adherence to the system just developed, every cycloparaffin system would be succeeded by a corresponding cyclo-olefine system having a like number of carbon atoms. However, in order to fully comprehend the hydroaromatic bodies, it is essential to know the aromatic compounds; therefore the discussion of the former will be deferred until the latter have been fully considered. The tricarbo-, tetracarbo-, and pentacarbocyclic compounds will be followed by the heptacarbocyclic derivatives, which are not very numerous, and lastly will appear the hexacarbocyclic compounds.

In many respects the aromatic bodies manifest a peculiar deportment, varying greatly from that of the aliphatic derivatives. However, the hydroaromatic compounds, and also the known tri-, tetra-, penta-, and heptacarbocyclic derivatives approach, in their chemical behavior, the saturated aliphatic substances, or, in case they contain pairs of doubly linked carbon atoms in the ring, they resemble the unsaturated aliphatic derivatives. Therefore, these classes of compounds, in contrast to the aromatic bodies, are designated aliphatic-cyclic or alicyclic saturated and

unsaturated compounds (B. 22, 769).

The study of carbocyclic derivatives has shown that the trimethylene ring can be more readily ruptured than the more stable pentamethylene or hexamethylene rings, whereas the latter are produced with greater difficulty. It is not certain whether octocarbocyclic bodies have really been prepared.

Similar phenomena have been encountered in the formation of certain heterocyclic aliphatic series—e. g., the lactones (1, 342), the lactams (1, 358), and the anhydrides of the dicarboxylic acids (1, 429), etc.

In presenting the oxy-acids (I, 334) a representation of the spacial arrangement or configuration of the carbon atoms was given; this was intended to account for the non-formation of a- and β -lactones, in comparison with the ease with which γ - and δ -lactones are produced.

The strain theory of A. v. Baeyer (B. 18, 2278; 23, 1275) has been proposed to explain the varying stability of the tri-, tetra-, penta-, and hexamethylene rings. This theory is based on the assumption that "the four valences of the carbon atom act in lines, which connect the center of a sphere with the solid angles of a regular tetrahedron inscribed within it, and hence form an angle of 109° 28' with each other." These four connecting lines are called the axes.

"The direction of attraction can suffer deviation; however, the magnitude of the latter has increasing tension as the consequence. The assumption of valence forces, acting at an angle, is excluded. The magnitude of the angle of deviation is the measure of the strain. In the case of ethylene the direction of attraction for the two valences of each carbon atom sustains an equally great deviation, until finally the directions have become parallel. The angle of deviation with ethylene is $\frac{109^{\circ} 28'}{2} = 54^{\circ}$ 44'. With trimethylene, which may be imagined to be an equilateral triangle, the angle made by the

methylene, which may be imagined to be an equilateral triangle, the angle made by the axes equals 60°, and the deviation of each, therefore, ½ (109° 28′ — 60°) = 24° 44′."

The following degictions are obtained in a similar manner.

The following deviations are obtained in a similar manner:

Tetramethylene
$$\frac{1}{2}$$
 (109° 28′— 90°) = 9° 44′
Pentamethylene $\frac{1}{2}$ (109° 28′— 108°) = 0° 44′
Hexamethylene $\frac{1}{2}$ (109° 28′— 120°) = -5° 16′.

It is, of course, presupposed that in the case of tetra-, penta-, and hexamethylene the carbon atoms lie in the same plane—the ring plane. The greatest deviation of the attraction of the two valences has occurred in dimethylene or ethylene. The greatest strain prevails in this body. It is the most unstable ring. It can be torn asunder not only by chlorine, bromine, and hydrogen bromide, but also by iodine. Trimethylene adds to itself with much more difficulty. Tetra-, penta-, and hexamethylene rings no longer behave like unsaturated bodies; they are quite stable in their behavior with chlorine, haloid acids, and potassium permanganate. The determination of the heat of combustion of the simplest cycloparaffins shows an appreciable fall from tri- to hexamethylene (B. 25, R. 496), which harmonizes with the views just expressed. The strain theory of v. Baeyer would indicate that the pentamethylene ring is more readily produced than the hexamethylene ring. This conclusion was the impulse that led to the execution of a series of successful experiments resulting in the formation of pentamethylene derivatives (consult B. 28, 655).

METHODS OF RING-FORMATION IN THE CASE OF CYCLO-PARAFFINS.

Methods allowing of the conversion of open carbon chains into closed carbon chains demand special consideration. *Nucleus-syntheses* were described as reactions by which carbon atoms, not previously in union with each other, were made to unite (vol. 1, 85); hence every transformation of an open chain into a closed carbon chain is a nucleus-synthesis. Indeed, there are well-known nucleus-synthetic methods which, applied to suitable aliphatic substances, lead to ring-formations with the production of cycloparaffins. These facts have already been mentioned at various places in the first volume of this book. They constitute the transition-reactions from the domain of the paraffins to that of the cycloparaffins. The most important of them are, therefore, axranged in a more tangible form:

1. Cycloparaffins are produced by the action of sodium (vol. 1, 84) upon dibromparaffins—the hydrobromic acid esters of the glycols:

2. Intramolecular Pinacone Formation.—Ditertiary glycols, the pinacones, are formed, together with secondary alcohols, in the reduction of ketones. Diacetyl pentane, when reduced, yields not only an aliphatic disecondary glycol, but a ditertiary glycol, a cyclic pinacone:

$$\begin{array}{c} \text{CH}_{\text{3}}\text{-CH}_{\text{3}}\text{-CH}_{\text{3}}\text{-CO} \cdot \text{CH}_{\text{3}} - \text{CH}_{\text{3}}\text{-CH}_{\text{3}}\text{-CH}_{\text{3}}\text{-CH}_{\text{3}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{-CH}_{\text{0}}\text{$$

3a. Intramolecular Acetoacetic Ester Condensation.—When sodium acts upon adipic ester, an intramolecular condensation corresponding to the acetoacetic ester formation takes place, and the product is a cyclic β -ketone carboxylic ester:

$$\begin{array}{c} \text{CH}_{1}.\text{ CH}_{2}.\text{ COOC}_{2}\text{H}_{5} \\ \text{CH}_{1}.\text{ CH}_{2}.\text{ COOC}_{3}\text{H}_{5} \\ \end{array} \xrightarrow{-\text{C}_{2}\text{H}_{5}\text{OH}} \begin{array}{c} \text{CH}_{1}.\text{ CH} \\ \text{CH}_{2}.\text{ CH}_{3} \end{array} \xrightarrow{\text{CO}} \begin{array}{c} \text{CO}.\text{ OC}_{2}\text{H}_{5} \\ \text{CH}_{3}.\text{ CH}_{3} \end{array}$$

3b. Oxalo-acetic Ester Condensation.—Diketopentamethylene dicarboxylic ester results from the action of sodium ethylate upon oxalic ester and glutaric ester:

$$\text{CH}_{\textbf{1}} < \!\!\!\!\! < \!\!\!\! \begin{array}{c} \text{CH}_{\textbf{1}} \cdot \text{CO}_{\textbf{2}} \text{C}_{\textbf{2}} \text{H}_{\textbf{5}} \\ \text{CH}_{\textbf{2}} \cdot \text{CO}_{\textbf{3}} \text{C}_{\textbf{3}} \text{H}_{\textbf{5}} \\ \end{array} + \left(\begin{matrix} \text{CO} \cdot \text{O} \cdot \text{C}_{\textbf{3}} \text{H}_{\textbf{5}} \\ \text{CO} \cdot \text{O} \cdot \text{C}_{\textbf{3}} \text{H}_{\textbf{5}} \\ \end{matrix} \right) = \text{CH}_{\textbf{2}} < \left(\begin{matrix} \text{C} \text{H}_{\textbf{-CO}} \\ \text{CH}_{\textbf{-CO}} \\ \text{CH}_{\textbf{-CO}} \\ \end{matrix} \right) \\ \leftarrow \text{CO}_{\textbf{2}} \text{C}_{\textbf{2}} \text{H}_{\textbf{5}} \\ \end{array}$$

Triketopentamethylene dicarboxylic ester is similarly formed from oxalic ester and acetone dicarboxylic ester.

4. Malonic Ester Syntheses and Acetoacetic Ester Syntheses.—Cycloparaffindicarboxylic esters (W. H. Perkin, Jr.) result from the action of alkylen bromides upon disodium malonic esters:

$$\begin{array}{c} CH_2Br \\ CH_3Br \\ CH_3 Br \\ CH_4 CCO_2C_2H_5)_2 = \\ CH_3 < CH_2 \\ CH_3 \\ CCO_2C_2H_5)_2 = CH_3 \\ CH_3 \\ CH_3 \\ CCO_2C_2H_5)_2 = CH_3 \\ CH_3 \\ CCO_3C_2H_5)_3 + 2NaBr \\ CH_4 \cdot CH_2Br \\ CH_3 \cdot CH_3Br \\ CH_3 \cdot CH_3Br \\ CH_4 \cdot CH_3 \\ CH_3 \cdot CH_3 \\ CH_4 \cdot CH_3 \\ CH_3 \cdot CH_3 \\ CH_4 \cdot CH_3 \\ CH_3 \cdot CH_$$

This reaction has been largely applied in the preparation of numerous trimethylene derivatives by merely substituting the brom- addition products of the olefine mono- and olefine dicarboxylic esters for the alkylen bromides. Thus, when sodium acetoacetic

٠4.

ester is allowed to act upon 1,4-dibrom-n-pentane, 1,2-methyl acetyl pentamethylene carboxylic ester is produced (B. 21, 742):

$$\begin{array}{c} \text{CH}_{1}.\text{ CHBrCH}_{3} \\ \text{CH}_{1}.\text{ CH}_{3}\text{Br} \end{array} + 2 \\ \begin{array}{c} \text{CHNa}.\text{ CO}_{1}\text{C}_{2}\text{H}_{5} \\ \text{CO}.\text{ CH}_{3} \end{array} = \\ \begin{array}{c} \text{CH}_{2}.\text{ CH}_{2} \\ \text{CH}_{3}.\text{ CH}_{3} \end{array} \\ \begin{array}{c} \text{CH}_{3} \\ \text{CO}_{1}.\text{ C}_{2}\text{H}_{5} \\ \text{COCH}_{3} \end{array} + \\ \begin{array}{c} \text{CH}_{3}.\text{ CO}_{2}\text{C}_{3}\text{H}_{5} \\ \text{CO}.\text{ CH}_{3} \end{array} \\ \begin{array}{c} \text{CH}_{3}.\text{ CO}_{2}\text{C}_{3}\text{H}_{5} \\ \text{CO}.\text{ CH}_{3} \end{array} + \\ \begin{array}{c} \text{CH}_{3}.\text{ CO}_{2}\text{C}_{3}\text{H}_{5} \\ \text{CO}.\text{ CH}_{3} \end{array} \\ \end{array}$$

 aa_1 -Dibrompimelic ester and sodium malonic ester form cyclopentene dicarboxylic ester, and not the expected hexamethylene tetracarboxylic ester. An exit of hydrobromic acid occurs:

$$CH_{1} < \underbrace{CH_{1} - CHBr \cdot CO_{1}C_{2}H_{\delta}}_{CH_{1} - CHBr \cdot CO_{2}C_{2}H_{\delta}} \xrightarrow{-2HBr} CH_{1} < \underbrace{CH_{1} - CCO_{2}C_{2}H_{\delta}}_{CH_{1} - CCO_{2}C_{2}H_{\delta}}$$

5. When iodine or bromine acts upon the disodium compounds of the alkylen dimalonic esters, upon disodium methylene, disodium ethylene dimalonic esters, etc., the sodium is withdrawn while a ring is simultaneously produced. This is analogous to the conversion of sodium malonic ester into diacetosuccinic ester and monosodium malonic ester into dimalonic ester by means of iodine. The resulting cycloparaffin tetracarboxylic acids split off two molecules of carbon dioxide and become cycloparaffin dicarboxylic acids (W. H. Perkin, Jr.):

$$\begin{array}{c} \operatorname{CH}_{3} < \overset{\operatorname{CNa}(\operatorname{CO}_{3}\operatorname{C}_{3}\operatorname{H}_{5})_{3}}{\operatorname{CNa}(\operatorname{CO}_{2}\operatorname{C}_{1}\operatorname{H}_{5})_{3}} & \to & \operatorname{CH}_{3} < \overset{\operatorname{C}(\operatorname{CO}_{3}\operatorname{C}_{3}\operatorname{H}_{5})_{3}}{\operatorname{C}(\operatorname{CO}_{2}\operatorname{C}_{3}\operatorname{H}_{5})_{3}} & \to & \operatorname{CH}_{3} < \overset{\operatorname{C}(\operatorname{H.CO}_{3}\operatorname{H}_{5})_{3}}{\operatorname{CH}_{2}-\operatorname{C}(\operatorname{CO}_{2}\operatorname{C}_{3}\operatorname{H}_{5})_{2}} & \to & \operatorname{CH}_{3} < \overset{\operatorname{C}(\operatorname{H.CO}_{3}\operatorname{H}_{5}\operatorname{H}_{5})_{2}}{\operatorname{CH}_{2}-\operatorname{C}(\operatorname{CO}_{2}\operatorname{C}_{3}\operatorname{H}_{5})_{2}} & \to & \operatorname{CH}_{3} \cdot & \operatorname{CH.CO}_{3}\operatorname{H}_{5}\operatorname{H}_{5} \\ & \overset{\operatorname{C}(\operatorname{H.CO}_{3}\operatorname{H}_{5}\operatorname{H}_{5})_{2}}{\operatorname{CH}_{3}-\operatorname{C}(\operatorname{CO}_{2}\operatorname{C}_{3}\operatorname{H}_{5})_{3}} & \to & \operatorname{CH}_{3} \cdot & \operatorname{CH.CO}_{3}\operatorname{H}_{5}\operatorname{H}_{5} \\ & & \operatorname{CH}_{3} \cdot & \operatorname{CNa}(\operatorname{CO}_{2}\operatorname{C}_{3}\operatorname{H}_{5}\operatorname{H}_{5})_{3} & \to \operatorname{CH}_{3} < \overset{\operatorname{C}(\operatorname{H.CO}_{3}\operatorname{H}_{5}\operatorname{H}_{5}\operatorname{H}_{5}}{\operatorname{CH}_{2}-\operatorname{C}(\operatorname{CO}_{2}\operatorname{C}_{3}\operatorname{H}_{5}\operatorname{H}_{5})_{3}} & \to \operatorname{CH}_{3} \cdot & \operatorname{CH.CO}_{3}\operatorname{H}_{5}\operatorname{H}_{5} \\ & & \operatorname{CH}_{3} \cdot & \operatorname{CH.CO}_{3}\operatorname{H}_{5}\operatorname{H}_{5} & & \operatorname{CH.CO}_{3}\operatorname{H}_{5}\operatorname{H}_{5} \\ & & \operatorname{CH}_{3} \cdot & \operatorname{CH.CO}_{3}\operatorname{H}_{5} \\ & & \operatorname{CH}_{3} \cdot & \operatorname{CH.CO}_{3}\operatorname{H}_{5}\operatorname{H}_{5} \\ & & \operatorname{CH}_{3} \cdot & \operatorname{CH.CO}_{3}\operatorname{H}_{5} \\ & & \operatorname{CH}_{3} \cdot &$$

The disodium compound of diacetyl adipic ester behaves similarly towards iodine.

6. Cyclic Ketone Formation.—Just as the calcium salts of the paraffin monocarboxylic acids, when heated alone, yield open-chain ketones, so do the calcium salts of some of the higher normal paraffin dicarboxylic acids afford cyclic ketones when they are subjected to dry distillation (J. Wislicenus):

7. Aliphatic diazo-bodies, like diazomethane and diazoacetic ester (1, 207), add themselves to olefine mono- and dicarboxylic esters, with the production of cyclic azo-derivatives or pyrazoline compounds, which

give up nitrogen quite readily and change to trimethylene compounds (E. Buchner):

$$N = N \quad CHCO_{2}C_{2}H_{6}$$

$$CH_{2} \quad CHCO_{2}C_{2}H_{6}$$

$$N = N \quad CHCO_{2}C_{2}H_{6}$$

$$CO_{2}C_{2}H_{6}CH \quad CH_{2}$$

$$CO_{2}C_{2}H_{6}CH \quad CH_{2}$$

I. TRI-, TETRA-, PENTA-, AND HEPTACARBO-CYCLIC COMPOUNDS.

This chapter will mainly consist of the cycloparaffins and their derivatives containing the number of carbon atoms indicated above. They are distinguished from their isomeric olefines in that they possess little power (sometimes lack it entirely) of combining with the halogens and haloid acids, and are quite stable toward potassium permanganate (B. 23, 704).

A. TRIMETHYLENE GROUP.

Trimethylene [Cyclopropane], $\begin{array}{c} CH_2 \\ CH_2 \end{array}$ > CH_2 , is a readily condensible gas. It is obtained by heating trimethylene bromide with metallic sodium (Freund, 1882), or by the action of alcohol and zinc dust (B. 20, R. 706).

It unites with more difficulty with bromine and hydriodic acid than propylene, CH₂= CH. CH₂. It is rearranged at a red heat into propylene (B. 29, 1297). It is not oxidized by potassium permanganate (B. 21, 1282).

Methyl Trimethylene boils at 4° (B. 28, 22). Vinyl Trimethylene, CH₂>CH- $\mathrm{CH} = \mathrm{CH_2}$, boils at 40°; its specific gravity is 0.73. It is formed in a peculiar manner by the action of alcohol and zinc dust upon the tetra-bromhydrate of pentaerythrol:

$$\begin{array}{c} \text{BrCH}_{\text{i}} > \text{C} < \overset{\text{CH}_{\text{i}}\text{Br}}{\text{CH}_{\text{i}}} > \text{C} < \overset{\text{CH}_{\text{i}}}{\text{CH}_{\text{i}}} \\ \end{array} \\ \begin{array}{c} \text{CH}_{\text{i}} > \text{C} < \overset{\text{CH}_{\text{i}}}{\text{CH}_{\text{i}}} \\ \end{array} \\ \begin{array}{c} \text{CH}_{\text{i}} > \text{C} < \overset{\text{CH}_{\text{i}}}{\text{CH}_{\text{i}}} \\ \end{array} \\ \begin{array}{c} \text{CH}_{\text{i}} > \text{C} < \overset{\text{CH}_{\text{i}}}{\text{CH}_{\text{i}}} \\ \end{array} \\ \begin{array}{c} \text{CH}_{\text{i}} > \text{CH}_{\text{i}} > \text{CH}_{\text{i}} \\ \end{array} \\ \begin{array}{c} \text{CH}_{\text{i}} > \text{CH}_{\text{i}} > \text{CH}_{\text{i}} \\ \end{array} \\ \begin{array}{c} \text{CH}_{\text{i}} > \text{CH}_{\text{i}} > \text{CH}_{\text{i}} > \text{CH}_{\text{i}} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \text{CH}_{\text{i}} > \text{CH}_{\text{i}} >$$

It yields a dibromide. Potassium permanganate oxidizes it to the corresponding glycol, CH₂>CH CHOH CH₂OH, which, by the further action of dilute nitric acid, becomes a-oxyglutaric acid (B. 29, R. 780).

Monochlor-trimethylene boils at 43° (B. 24, R. 637). Dichlor-trimethylene

boils at 74° (B. 25, 1954).

Acetyltrimethylene, CH₂ CH . CO . CH₃, boils at 113°. (See acetotrimethylene carboxylic acid, p. 23.)

Trimethylene Carboxylic Acids (A. 284, 197) are obtained by the general methods 4 and 5, and also by method 7 (p. 21), which is only suitable for the preparation of trimethylene derivatives. The trimethylene polycarboxylic acids, which contain two carboxyls linked to one carbon atom, split off carbon dioxide and pass into acids containing less carboxyl. Remarkable isomeric phenomena are due to the arrangement of the carboxyl groups upon the same or different sides of the plane assumed by the trimethylene ring. This is similar to the isomerism of the trithioaldehydes (1, 203). Trimethylene Carboxylic Acid, C₃H₅. CO₃H, melting at 18° and boiling at 183°, is isomeric with crotonic acid. It is produced, together with butyrolactone, by heating

Trimethylene-1,1-dicarboxylic Acid (Vinaconic Acid), $\frac{CH_2}{CH_2}$ >C(CO₂H)₂, melting at 140° (see method 4, p. 20). Hydrobromic acid converts it into brom-ethylmalonic acid, BrCH₂. CH₂. CH($\frac{CO_2H}{CO_2H}$). It also unites with bromine (B. 18, 3314). It is not altered by nitric acid, potassium permanganate, or by nascent hydrogen (B. 23, 704; 28, 8). The esters of vinaconic acid condense to butane tetracarboxylic esters with sodium malonic ester. In this respect it deports itself like the a,β -olefine carboxylic esters (vol. I, and B. 28, R. 464). Consult A. 294, 89, for the constitution of vinaconic acid and the homologue—Methyl Vinaconic Acid.

Trimethylene-1,2-dicarboxylic Acid is known in two isomeric modifications, called the cis- and cis-trans forms (A. 245, 128):

Cis-Trimethylene-1,2-dicarboxylic Acid melts at 139°; its anhydride at 59°. The acid is produced when trimethyl-1,2-tri- and 1,2-tetracarboxylic acids are heated. Cis-trans-Trimethylene-1,2-dicarboxylic Acid melts at 175°; its methyl ester, boiling at about 210°, is obtained, together with glutaconic ester, from acryldiazoacetic ester by method 7, p. 21, and by the action of diazomethane upon fumaric ester (B. 27, 1888; 28, R. 290).

28, R. 290).

Trimethylene-1,2-tricarboxylic Acid, CH₂<\(\frac{C(CO_2H)_2}{CHCO_2H}\), melts at 187°, with decomposition. Its ethyl ester, boiling at 276°, is obtained from aβ-dibrompropionic ester by method 4, p. 20 (B. 17, 1187), and from a-bromacrylic ester (B. 20, R. 140, 258).

Sym. Trimethylene-1,2,3-tricarboxylic Acid, CO₂H.CH< CH.CO₂H. The cis-form melts at 150-153°; the cis-trans form melts at 220°. The anhydride melts at 187° and boils at 265°. The cis-acid is derived from 1,2,3-tetracarboxylic acid (B. 17, 1652), the cis-trans form from fumaric-diazoacetic ester (B. 23, 2583). See B. 27, 868, for alkyltrimethylene tricarboxylic acids.

for alkyltrimethylene tricarboxylic acids.

Trimethylene-1,2-tetracarboxylic Acid, CH₂ < C(CO₂H)₂, is converted at 200° into the anhydride of cis-1,2-dicarboxylic acid. Its ethyl ester, melting at 43° and boiling at 187° (12 mm.), is produced according to method 5, p. 21 (B. 23, R. 241).

Trimethylene-1,2,3-tetracarboxylic Acid, (CO₂H)₂C< CH. CO₂H, passes at 95–100° into cis-1,2,3-tricarboxylic acid. Its *ethyl ester*, boiling at 246°, is obtained by method 4 (p. 20) from dibromsuccinic ester. The *cis-*1,2, *trans-*1,3-Acid decomposes at 196–198° (B. 28, R. 290).

1,1-Dimethyl-2,3-trimethylene Dicarboxylic Acid, (CH₃)₂C

CH . CO₂H

is probably caronic acid, a decomposition product of carone, a ketone of the terpene group (see this). It can be readily changed to terebic acid (see this).

Aceto-trimethylene Carboxylic Acid, $\frac{\text{CO}_3\text{H}}{\text{CH}_3\text{CO}}$ CC $\frac{\text{CH}_3}{\text{CH}_4}$, decomposes at 200° into CO₂ and aceto-trimethylene. Its ester is formed from ethylene bromide and sodium acetoacetic ester (B. 17, 1440).

Disceto-adipic ester results simultaneously. The ester boils at about 195°.

melts at 200° (see C(CO₂H) Methylcyclopropen-dicarboxylic Acid, CH2. CH< B. 26, 750).

B. TETRAMETHYLENE GROUP.

The methods 1, 4, and 5, producing ring-formations, have been applied in the preparation of tetramethylene derivatives.

CH₂. CHCH₃, boiling at 39-42°, is obtained by means Methyl-tetra-methylene, CH₂.CH₂ of method I, p. 20.

Amido-tetramethylene, C4H7. NH2, boiling at 81°, results in the action of bromine

and caustic potash upon tetramethylene carbonamide. Nitrous acid changes it to Oxy-tetramethylene, C₄H₇. OH, boiling at 123°, which, acted upon with concentrated hydrobromic acid, sustains a rupture of its ring with the production of its bromide (boiling point, 103°) and 1,3-dibrombutane, CH₂Br. CH₂. CHBr. CH₃ (J. Ch. Soc. 65, 950).

Tetramethylene-methylamine, C₄H₇. CH₂. NH₂, boiling at 83°, is prepared by

reducing the nitrile of tetramethylene carboxylic acid.

Tetramethylene-methyl Carbinol, C4H, CH(OH). CH, from the corresponding ketone, boils at 144°.

Tetramethylene-diethyl Glycol, [C, II, C(OH)C, II,]2, obtained by the reduction of tetramethylene ethyl ketone, melts at 95°

Tetramethylene-methyl- and ethyl Ketones, boiling at 135° and 145°, have been prepared from the acid chloride by action of zinc alkyls (B. 25, R. 371).

Ditetramethylene Ketone, (C, II,), CO, boiling at 205°, is prepared from the cal-

cium salt of the carboxylic acid. Tetramethylene Carboxylic Acid, C₄H₇CO₂H, boiling at 194°, smells like a fatty acid, and is obtained from the 1-dicarboxylic acid. Its ethyl ester boils at 160°; its chloride boils at 142°; its anhydride at 160°; while the amide melts at 130°, and the nitrile boils at 150° (B. 21, 2692).

Tetramethylene-1, I-dicarboxylic Acid melts at 155°, and then reverts to the monocarboxylic acid. Its cthyl ester boils at 224°, and is produced by method 4, p. 20. Cis-Tetramethylene-1,2-dicarboxylic Acid, melting at 137°, is obtained from the tetracarboxylic acid. Its anhydride melts at 77° and boils at 271° (B. 26, 2243). The trans-acid, melting at 131° (B. 27, R. 734), is produced when the preceding acid is heated to 1900 with hydrochloric acid.

Bromine and phosphorus produce 1,2-dibromtetramethylene dicarboxylic acid, the ester of which is converted by alcohol and potassium iodide into the ester of Cyclobutene

CH₂—C. CO₂H | " | " , which melts at 178° with decomposition, and CH2—CCO2H Dicarboxylic Acid, readily changes to its anhydride (J. Ch. Soc. 65, 950).

Tetramethylene-1,3-dicarboxylic Acid.—See A. 256, 198.

Diaceto-tetramethylene Dicarboxylic Ester is produced according to method 5, p. 21 (B. 19, 2048).

Tetramethylene-1,2-tetracarboxylic Acid melts at 145-150°, when it changes into the cis-1,2-dicarboxylic acid. Its ester is obtained by method 5, p. 21.

сн. >сн. со.-Tetramethylene-1,3-diglyoxylic Acid, COOH . CO . CH < CH,

COOH, melting at 240°, is produced in the condensation of pyroracemic acid and paraformaldehyde with concentrated sulphuric acid. It is decomposed when heated with alkalies into ethylene and oxalic acid, and by concentrated sulphuric acid into a dilactone (B. 29, 2273).

The truxillic acids, found among the secondary alkaloids of cocaine, are regarded as diphenyl tetramethylene dicarboxylic acids (see alkaloids).

See pinene for the view that it is a derivative of a combined hexa- and tetra-

-e.g., pinonic acid, pinic acid, norpinic acid-are derivatives of tetramethylene.

C. PENTACARBOCYCLIC COMPOUNDS.

The number of known pentacarbocyclic derivatives is much greater than that of the tri- and tetracarbocyclic compounds. They are derived in part from cyclopentane or pentamethylene, and in part from cyclopentenes. Cyclopentane and its derivatives have been obtained not only by the ring-synthetic methods 1, 3, 4, 5, and 6 (pp. 20, 21), but also from hexacarbocyclic ring-shaped ortho-diketones by an intramolecular atomic rearrangement—e. g., benzilic acid from benzil (1, p. 54); see below—chlordiketopentamethylene. This second reaction will be again presented in the decomposition of aromatic bodies (see these). Furthermore, hexaoxybenzene has yielded remarkable pentamethylene derivatives: croconic acid and leuconic acid. They will be discussed later in connection with hexaoxybenzene.

Camphor can be readily rearranged into aromatic derivatives, and should probably be regarded as a derivative of the hydrocarbon,

methylene derivatives—e. g., camphorphorone and camphoric acid. Camphor and its cyclic transformation products will not be considered until after the benzene derivatives, along with the terpenes, under the hydroaromatic bodies.

T. Hydrocarbons. Pentamethylene, R-Pentene [Cyclo-Pentane] CH₂. CH₂, CH₂, boiling at 50°, is obtained by the reduction of pentamethylene iodide. Methyl pentamethylene, boiling at 75°, is made from 1,5-dibrom n-hexane. 1,2-Methyl-ethyl-cyclopentane boils at 124°. 1,3-Dimethyl Pentamethylene, from the corresponding ketone (B. 29, 403), boils at 93°.

Cyclopentene, CH CH₂. CH₂, boiling at 45°, is prepared by the action of caustic potash upon pentamethylene iodide (A 275, 331), and Perchlorcyclopentene, C₈Cl₈, melting at 41° and boiling at 283°, by acting with PCl₅ upon perchlor-ketocyclopentenon (B. 23, 2214).

Methylcyclopentene, CH CH₂. CH₂, boiling at 70°, and obtained from 3-methylcyclopentanol by means of zinc chloride (B. 26, 775), yields methylglutaric acid upon oxidation.

Cyclopentadiëne, Pentol (B. 22, 916), CH₂ CH = CH boiling at 41°, is present

in the crude benzene from coal tar. It is a colorless liquid. Both acids and alkalies attack it energetically. It reduces an ammoniacal silver solution. It forms addition products with one and two molecules of the halogens and haloid acids—e. g., monochlorcyclopentene, C_5H_1Cl , boiling at 50° (40 mm.), trichlorcyclopentane, $C_5H_5Cl_3$, boiling at 196° , and tetrachlorcyclopentane, $C_5H_6Cl_4$, boiling at 94° (15 mm.). It polymerizes readily on standing to a dimolecular compound, $(C_5H_6)_3$, which at the ordinary temperature boils at 170°, with partial return to the monomolecular body, and without decomposition at 88° (35 mm.). It is much more stable than the simpler compound, and recalls the terpenes in its behavior (B. 29, 552).

- 2. Alcohols.—Cyclopentanol, C₅H₉OH, boils at 139°. Its bromide boils at 137°, the iodide at 164°, and the amine at 107° (A. 275, 322). [3-Methylcyclopentanol], CH₂.CH . CH₃, boils at 49° (12 mm.), and the amine at 42° (12 mm.) (B. 25, 3519; 26, 775). Both alcohols have been prepared by the reduction of their corresponding ketones.
- 2-Methylcyclopentanol, HO.CH< CH₂ CH₃ CH₃, from [methylcyclopentenon], boils at 148°.
- 3. Ketones.—The cyclic ketones, obtained from calcium adipate and β -methyl-adipate, according to method 6 (p. 21), constitute the starting-out material for the preparation of the corresponding alcohols, from which the saturated and unsaturated pentacarbocyclic hydrocarbons are subsequently prepared. Adipinketone [Cyclopentanon], keto-pentamethylene, CO $\stackrel{\text{CH}_1}{\subset}$ CH $_1$, boiling at 130°, occurs in "wood oils," and results from the saponification of 2-ketopentamethylene carboxylic ester (p. 28). It has an interpretable of the saponification of 2-ketopentamethylene carboxylic ester (p. 28).

from the saponification of 2-ketopentamethylene carboxylic ester (p. 28). It has an odor like that of peppermint, and yields glutaric acid when it is oxidized. Its oxime melts at 120° (A. 275, 312). It condenses with benzaldehyde to a mono- and a dibenzal compound, $C_6H_5CH:(C_5H_6O)$ and $C_6H_5CH:(C_5H_6O):CHC_6H_5$ (B. 29, 1601, 1836). Sodium ethylate condenses two and three molecules of cyclopentamon to cyclopentampentamon, $(C_5H_6O):(C_5H_6)$, boiling at 118° (12 mm.), and cyclodipentampentamon, $(C_5H_6):(C_5H_6):(C_5H_6)$, melting at 77° and boiling at 190° (12 mm.) (B. 29,

cyclopentanpentanon, $(C_6H_6O): (C_5H_6)$, boiling at 118° (12 mm.), and cyclodipentanpentanon, $(C_5H_6): (C_5H_6)$, melting at 77° and boiling at 190° (12 mm.) (B. 29, 2962). 3-Methylcyclo-pentanon, $CO < \frac{CH_2 \cdot CHCH_3}{CH_3 \cdot CH_3}$, boiling at 142° (B. 25, 3517), smells like camphorphorone (see this), which also, like tanacetophorone, belongs

3517), smells like camphorphorone (see this), which also, like tanacetophorone, belongs to the cyclopentations. These last-mentioned phorones will be treated after camphor. A 2-Methylcyclopentanon, which also boils at 142-144°, has been prepared from a-methyladipic acid (B 29, R. 1115). 2,5-Dimethylcyclopentanon, boiling at 146°, is obtained from aa₁-dimethyladipic acid (B. 29, 403).

Methylcyclopentenon, CH₃. CCO. CH₂, boiling at 157°, occurs in wood-oil. Its

oxime melts at 128° (B. 27, 1538). Hexachlorketo-R-pentene, $\frac{\text{CCl}_2}{\text{CCl}} = \frac{\text{CCl}_2}{\text{CCl}} > \text{CO}$,

melting at 31°, boiling at 156° (80 mm.), and CCl. CCl₂ CO, melting at 92° and boil-Ccl. CCl₂ ing at 148° (75 mm.), result upon oxidizing the corresponding a-oxyacids, prepared from o-amidophenol and pyrocatechol, with chromic acid (B. 24, 926; 25, 2697).

Mono-, di-, and trichlor-o-diketopentamethylenes are obtained, in a manner similar to the chlorinated keto-R-pentenons, from phenol and chloranilic acid. Hydrogen sulphide converts the monochlordiketopentamethylene into a-thiophenaldehyde (see this), and ammonia changes it to chlorpyridine (B. 22, 2827). Potassium chloranilate, acted upon with chlorine or bromine and water, yields Trichlortriketopentamethylene,

used (p. 46) (B. 24, 916; 25, 2225).

The primary decomposition products of the benzenes applied in these reactions are mainly chlorinated ketonic acids—ε. g., in the last instance we obtained from resorcinol the acid, CCl₂. CO. CCl.: CCl. CCl₃COOH, perchloracetyl crotonic acid, which, heated with concentrated sulphuric acid, forms the ring of ketopentamethylene (B. 26, 513). Similarly, β,δ-dibrom lævulinic acid, CH₂Br. CO. CHBr. CH₂. COOH, when treated with fuming sulphuric acid, is converted into two dibromdiketo-R-pentenes, CBr—CO

CH—CO

CH—CO

CH—CO

CH—CO

CH—CO

CH—CO

CH—CO

CH—CO

Pentaketopentamethylene is leuconic acid (p. 25). It is produced by oxidizing

croconic acid.

4. Carboxylic Acids.—Cyclopentan-carboxylic Acid, CH₂. CH₃ CH . CO₂H, boiling at 214°, has a disagreeable, sweat-like odor. It has been prepared from the a-oxyacid (A. 275, 337). Cyclopentan-acetic Acid, C₅H₉. CH₂. COOH, is an oil boiling at 140° (26 mm.). It is obtained from cyclopentanmalonic ester, the condensation product of pentamethylene iodide and sodium malonic ester (B. 29, 1997).

densation product of pentamethylene iodide and sodium malonic ester (B. 29, 1997).

CH₂. CH(CH₃)

2-Methylcyclopentan-carboxylic Acid, CH₂. CH₂—>CH. CO₃H, boiling at 219°, is produced when potassium hydroxide acts upon the a-acetyl body (p. 28).

Both monocarboxylic acids may be obtained from the corresponding t-dicarboxylic

acids

Cyclopentan-I-dicarboxylic Acid, CH₂. CH₂ C(CO₂H)₂, melting at 177°, and 2-Methylcyclopentan-I-dicarboxylic Acid, melting at 174°, whose esters have been prepared according to method 4, p. 20 (B. 26, 2246; 27, 1228). The cyclopentan-I, 2-dicarboxylic acid is known in two modifications. The cis-form yields an anhydride. It is obtained by heating (B. 18, 3246) the cyclopentan-I, 2-tetracarboxylic acid, prepared according to method 5 (p. 21).

CH₂—C. COOH

Cyclopentene Dicarboxylic Acid, CH₂

CH₂—C. COOH

CH₂—C. COOH

CH₂—dibrompimelic acid, and by treating

sults from the action of sodium alcoholate upon a,a_1 dibrompimelic acid, and by treating 1,2-dibromcyclopentan-1,2-dicarboxylic acid (produced in the bromination of cyclopentan-dicarboxylic acid) with alcohol and potassium iodide. It takes up 2Br readily. It forms adipic acid by fusion with caustic potash (B. 28, 655).

Camphoric acid, probably 2-dimethylcyclopentan-1 3-dicarboxylic acid, will be discussed together with camphor. An ethyl cyclopentene carboxylic acid has been de-

tected among the decomposition products of ecgonine (see this).

5. Alcohol Carboxylic Acids.—

a-Oxycyclopentan-carboxylic Acid, $CH_2-CH_2 > CC_2H$, melting at 103°, is obtained from cyclopentanon, CNH, and hydrochloric acid (A. 275, 333). It yields pentamethylene carboxylic acid by reduction. Hexachlor-a-oxycyclopentene carboxylic Acid, $CCI_2-CCI_2 > CC_2H$, results from the action of sodium carbonate or sodium acetate upon the chlorinated cyclohexene-o-diketone. When it is heated, it rearranges itself into an isomeric acid (B. 23, 824). Boiling water converts both acids CCI = CCI - CCI

 $\begin{array}{c} C(OH) - CCl_2 \\ CCl - CH_2 \\ CCl - CH_2 \\ \end{array}, \ \ is \ \ produced \ \ when \ \ chlorine \ \ acts \\ upon \ \ an \ \ alkaline \ phenol \ solution \ (B.\ 22,\ 2827). \end{array}$

6. Ketone Carboxylic Acids .-

2-Ketopentamethylene-carboxylic Ester, CH₂. CH₂ CO₂C₂H₅, is obtained from adipic ester by method 5 (p. 21). It forms ketopentamethylene when it is saponified.

1, 2-Methylacetyl-pentamethylene-carboxylic Ester, CH₂. CH₂. CH₃.

is prepared from 1,2-dibrom-n-pentane according to method 4, p. 20 (B. 21, 742).

Symmetrical Ketopentamethylene-carboxylic Acid, CO

CH₂. CHCO₂H

CH₂. CHCO₂H

melting at 189°, is obtained from aconitic ester and sodium malonic ester (B. 26, 373). Cyclo-

pentan-2,3-dion-1,4-dicarboxylic Ester, CH₂ CH.CO , is produced ac-

cording to method 3 (p. 20) from n-glutaric ester and oxalic ester (B. 27, 1353). Tri-ketocyclopentan-dicarboxylic Ester, $CO-CH > CO_2C_2H_5$, is formed from acetone dicarboxylic ester and oxalic ester (B. 29, R. 1117). Diphenylketocyclopentene Acetic Acid, C_6H_5 . $C - CH > CO_2C_3H_5$ is obtained from benzil and lævulinic acid.

D. HEPTACARBOCYCLIC COMPOUNDS.

The most important members of this series have been obtained from suberone. The ease with which the ring containing seven members passes into the "six-membered" ring is an argument in favor of the view that the ring-formation with carbon atoms reaches its limit with the "seven-membered" derivatives. Compare further A. 275, 363.

Suberane, Heptamethylene, Cycloheptane, CH₂. CH₂. CH₂. CH₂, boiling at 117°, results from the reduction of suberyl iodide. Bromine and aluminium bromide change suberane to pentabromtoluene (see this), whereas when it is heated with hydriodic acid, it is converted into methylcyclohexane or hexahydrotoluene (B. 27, R. 47). Suberylene, Cycloheptene, boiling at 114°, is produced by the action of caustic potash upon suberyl iodide. Caustic potash converts its dibromide into cycloheptadiëne, heptamethylene terpene, C, H₁₀, boiling at 121° (B. 29, R. 89). Suberyl Alcohol, C₆H₁₂. CHOH, boiling at 184°, results from the reduction of suberone. Its chloride boils at 174°, and its amine at 169° (B. 26, R. 813).

Suberone, Cycloheptanon, CH₂. CH₂. CH₂>CO, boiling at 180°, has an odor like that of peppermint. It is produced in the distillation of calcium suberinate. It yields pimelic acid when it is oxidized. It condenses with benzaldehyde (B. 29, 1600). Its oxime melts at 23° and boils at 230°.

Suberan-carboxylic Acid, $C_7H_{18}CO_2H$, is a colorless liquid. It results when suberenic acid, $C_7H_{11}CO_2H$, melting at 53°, is reduced by sodium amalgam. This latter acid is produced when alcoholic potash acts upon the liquid chlorsuberonic acid. The ester of Suberane-1,1-dicarboxylic Acid may be synthesized from hexamethylene

bromide and sodium malonic ester. It loses CO₂ and becomes suberanic acid (B. 27,

R. 735).

Oxysuberanic Acid, Suberyl Glycollic Acid, C₇H₁₂(OH)CO₂H + ½H₂O, melts, when anhydrous, at 89°. It is formed when prussic acid and hydrochloric acid act upon suberone. Concentrated hydrochloric acid converts it into chlorsuberonic acid (A. 211,

117). 1,2-Dimethyl-1,2-dihydroxyheptamethylene, CH₂ CH₂ . CH₂ . C(OH) . CH₃ is obtained from diacetyl pentane by method 2 (p. 20).

II. HEXACARBOCYCLIC COMPOUNDS.

The chemistry of the hexacarbocyclic derivatives has been much more fully and richly developed than that of the ring-systems which have been discussed in the preceding section. The hexacarbocyclic compounds are classified as follows:

- A. Aromatic or Benzene derivatives containing a single nucleus.
- B. Hydroaromatic substances containing a single nucleus.
 This class contains the terpene and the camphor groups.
- C. Aromatic substances containing several nuclei. The parent hydrocarbons of this group contain (a) several benzene residues combined directly to each other, or by means of aliphatic hydrocarbon residues; or, (b) two (or more) nuclei so linked to one another that they have two carbon atoms in common (twin nuclei, condensed nuclei):

Numerous derivatives of almost every imaginable kind can be referred to each of these hydrocarbons,—a domain of immeasurable expansibility. Many of these bodies, particularly naphthalene and its derivatives, are likewise followed by a series of hydro-bodies, which will not, however, be discussed as a fourth class, but always directly after the non-hydrogenized compounds of the respective hydrocarbon.

A. AROMATIC COMPOUNDS OR BENZENE DERIVA-TIVES CONTAINING A SINGLE NUCLEUS.

The aromatic compounds are mostly obtained from aromatic oils and resins. They differ in various respects from the members of the fatty or marsh-gas series, but are principally distinguished from the latter by their greater carbon content. The theoretical representations upon their constitution are based chiefly on the views developed by Kekulé in 1865—Kekulé's benzene theory. The views of this investigator are in brief as follows (compare Kekulé, Lehrbuch der org. Chemie, 2, 493; A. 137, 129):

1. All aromatic compounds are derived from a nucleus consisting of six carbon atoms; its simplest compound is benzene, C₆H₆. All other aromatic derivatives may be obtained from the latter by substituting other atoms or atomic groups (side-chains) for its hydrogen atoms. The new derivatives are distinguished from the methane compounds by their specific benzene character, and are, therefore, called benzene derivatives.

2. Benzene has a symmetrical constitution. Each carbon atom is combined with one hydrogen atom. Differences between the individual C- and H-atoms have not been discovered (similar to the polymethylene derivatives). Isomerides are, therefore, only possi-

ble when two or more side-chains are present.

3. The structure of the benzene nucleus is such that the six carbon atoms, or CH-groups, form a *closed*, *ring-shaped* chain, the atoms being joined alternately by single and double bonds:

In benzene, C_eH_e, the fourth affinity of each C-atom is joined to hydrogen; in the benzene derivatives it is combined with other atomic groups.

THE BENZENE DERIVATIVES.

The benzene derivatives can be obtained by the replacement of hydrogen in benzene, just as the aliphatic substances can be derived from methane. Those members containing carbon side-chains can be derived from benzene, and by their decomposition, or by the splitting-off of the side-chains, they revert to benzene. The stability of the benzene nucleus distinguishes the aromatic substances from the methane derivatives. Thus, oxidation, and also reduction, which leads finally to cyclohexane derivatives or hexahydrobenzene bodies, may be carried on, as a general thing, without tearing the ring asunder. Therefore, reduction unites the benzene bodies to the cyclohexane derivatives (p. 18).

Solid benzene bodies are distinguished at the ordinary temperature by their crystallizing power. This accelerates experimental work very materially.

The hydrogen of benzene can be very readily replaced by the halogens and the nitro (NO₂) and sulpho (SO₃H) groups:

Mono-, di-, tri-, tetra-, penta-, and hexa-derivatives of benzene result, depending upon whether one, two, three, four, or more of the hydrogen atoms of benzene are replaced. The production of nitro compounds by the direct action of nitric acid is particularly characteristic of the benzene derivatives, whereas the fatty compounds are generally oxidized and decomposed.

In the reduction of the nitro-derivatives we obtain the amido-com-

pounds:

Amidobenzene
$$C_6H_5$$
, NH_2 C_6H_4 (NH_2)₂ C_6H_3 (NH_2)₃.

Aniline

The so-called azo-derivatives appear as intermediate products of the reaction, whereas when nitrous acid acts on the amido-derivatives the diazo-compounds result. Both classes are of exceptional occurrence in the methane series (1, p. 172).

By introducing hydroxyl for hydrogen into benzene we obtain the *phenols*, which may be compared to the alcohols:

$$\begin{array}{cccc} C_6H_5 \cdot \mathrm{OH} & C_6H_4(\mathrm{OH})_2 & C_8H_3(\mathrm{OH})_3 \\ \mathrm{Phenol} & \mathrm{Dioxybenzene} & \mathrm{Trioxybenzene.} \\ \mathrm{(Carbolic \ Acid)} & & & & & \end{array}$$

These resemble the tertiary alcohols in having the group C. OH attached to the three carbon affinities (1, p. 110), hence on oxidation they cannot yield corresponding aldehydes, ketones, or acids.

The benzene residue diminishes the basic properties of the amido-group and increases the acid nature of the phenol hydroxyl. It has a more negative character than the residues of the aliphatic hydrocarbons.

The entrance of univalent paraffin, olefine, and acetylene residues into benzene produces *homologues* of the latter, both saturated and unsaturated:

In these hydrocarbons the benzene residue preserves the specific properties of benzene; its hydrogen can readily be replaced by halogens and the groups NO₂ and SO₂H. On the other hand, the side-chains behave like the hydrocarbons of the fatty series; their hydrogen can be replaced by halogens, but not by (by action of HNO₂ or H₂SO₄) the groups NO₂ and SO₂H. Different isomeric derivatives are possible, depending upon whether the substitution of the halogens (or other groups) has occurred in the benzene residue or the side-chains—e. g.:

The halogen atoms in the benzene residue are very firmly combined and mostly incapable of double decomposition, while those in the sidechains react exactly as in the methane derivatives.

The substitution of hydroxyl for the hydrogen of the side-chains leads to the true alcohols of the benzene series:

C₆H₆.CH₂.OH Benzyl Alcohol

 C_4H_5 . CH_4 . CH_4 . OHPhenyl Ethyl Alcohol

 $C_{\epsilon}H_{\epsilon} < \stackrel{CH_{3}}{CH_{2}}$. OH Tolyl Alcohol.

The primary class is oxidized to aldehydes and acids:

CaHa. CHO Benzaldehyde

 C_6H_5 . CH_2 . CHOPhenyl Acetaldehyde

 $C_{\bullet}H_{\bullet}<_{CHO}^{CH_{\bullet}}$

The acids in which the COOH group is joined to benzene can be formed by introducing carboxyl groups directly into benzene, or by oxidizing the homologues of the latter:

C₆H₆. CO₂H Benzene Carboxylic Acid Benzene Dicarboxylic Acid Benzene Tricarboxylic Acid

 $C_4H_4(CO_2H)_2$

 $C_4H_3(CO_2H)_3$

 $C_{\bullet}H_{\bullet}<_{CO_{\bullet}H}^{CH_{\bullet}}$

 C_6H_5 . CH_2 . CO_2H

 $C_{\bullet}H_{\bullet}<_{CO_{\bullet}H}^{CO_{\bullet}H}$

Phenylacetic Acid

The hydrogen of the benzene residue in these acids, as well as in the alcohols and aldehydes, is replaceable by halogens, and the groups NO₂, SO,H, OH, etc.

Benzene is the basis in the preceding explanation. The various benzene derivatives having aliphatic side-chains are all regarded as substitution products of benzene. It is plain, however, that this manner of presentation can be reversed. Then the deriva-tives of benzene with one side-chain would be, for example, phenyl substitution products of aliphatic bodies, as indicated in the following designations:

C₆H₅CH₂. CH₂. CO₂H Phenyl propionic acid.

ISOMERISM OF THE BENZENE DERIVATIVES.*

Proof of the Equivalence of the Six Hydrogen Atoms in Benzene.—Let any one hydrogen atom in benzene be replaced by another atom, or atomic group, and every resulting compound can exist in but one modification; thus there is but one chlorbenzene, one nitrobenzene, one amidobenzene, one toluene, one benzoic acid, etc. The following compounds are known in but one modification:

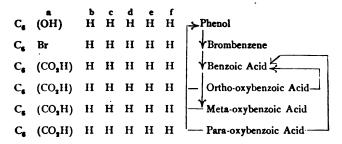
$$C_6H_5Cl,\ C_6H_5(NO_2),\ C_6H_5\cdot NH_2,\ C_6H_5\cdot CH_8,\ C_6H_5\cdot CO_2H,\ \text{etc.}$$

^{*}Theorie der aromatischen Verbindungen v. A. Ladenburg, 1876.

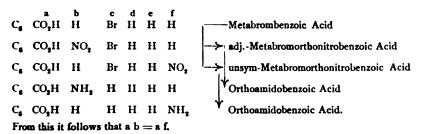
The six hydrogen atoms of benzene are of equal value, just the same as the four hydrogen atoms of methane (1, p. 37). Benzene has a symmetrical structure.

This equivalence of the six hydrogen atoms is very important for the theory of the benzene derivatives, and was demonstrated beyond question by Ladenburg in 1874 (B. 7, 1684; 8, 1666).

1. If phenol be converted into brombenzene, and this in turn be changed by sodium and carbon dioxide into benzoic acid, the carboxyl group of the benzoic acid will take the place of that hydrogen atom in benzene which was held by the hydroxyl in phenol. Furthermore, three monoxybenzoic acids are known; of these the metaoxybenzoic acid is produced from benzoic acid, while the ortho- and para-oxybenzoic acids can be converted into benzoic acid (A. 132, 151, 309). The three oxybenzoic acids (the significance of the prefixes ortho-, meta-, and para- will be explained further on in connection with the benzene diderivatives) yield the same phenol, which is therefore produced by the replacement of four different hydrogen atoms of benzene by the hydroxyl group. Consequently, four hydrogen atoms of benzene are equivalant:



2. Two pairs of hydrogen atoms are symmetrically arranged with reference to one hydrogen atom in benzene—i. e., the replacement of each of the two hydrogen atoms of a pair by the same atom or atomic group will give rise to the same body. This statement in regard to the one pair, b and f, is evident from the formation of the same orthomidobenzoic acid from the two different nitrobrombenzoic acids, which are obtained in the nitration of metabrombenzoic acid (Hübner and Petermann, A. 149, 129; 222, 111; B. 2, 140):



The proof for the second pair is found in the preparation of metabromtoluene from two bromine derivatives (Wroblewsky, A. 192, 213; A. 234, 154), in which the bromine has replaced two different hydrogen atoms, which, therefore, are symmetrically arranged:

a c = a e, with reference to the hydrogen replaced by the methyl group of toluene:

ŧ

When this bromtoluene is oxidized it changes to the same metabrombenzoic acid which is employed as the starting-out material for the preparation of the adj.- and unsym.-metabromorthonitrobenzoic acid. Hence it follows that in the latter proof the bromine replaces two different hydrogen atoms from those previously replaced by the amido group of the orthoamidobenzoic acid, and, consequently, there are present in benzene not only one, but also two pairs of hydrogen atoms, which are symmetrically arranged with reference to one hydrogen atom, which would thus prove the equal value of the six hydrogen atoms in benzene (compare also Ladenburg, B. 10, 1218).

The proof of the symmetrical arrangement of the second pair of hydrogen atoms may be added to the preceding presentations in regard to the first pair. It is as follows: Orthoamidobenzoic acid, obtained in two different ways (p. 33), can be changed to the same oxybenzoic acid—salicylic acid. When the latter is nitrated it yields two different mononitrosalicylic acids. On heating the diethyl ethers of these acids with ammonia, both ethoxyl groups are replaced by amido-groups, and free nitroamidoacids are then liberated from the nitroamidobenzamides. Nitrous acid and alcohol change the nitroamidobenzoic acids into the same nitrobenzoic acid. As this acid, obtained from the two different nitrosalicylic acids, yields an amidobenzoic acid (meta), which differs from the amidobenzoic acid that gave the salicylic acid, and as it affords an oxybenzoic acid (meta), differing from salicylic acid, there must be two additional hydrogen atoms in benzene which are symmetrically arranged with reference to the one replaced by the CO₂H group:

But one place, therefore, remains for the third oxybenzoic acid, the paraoxybenzoic acid, and this place—the so-called para-place or position—is possible only once in benzene.

The six hydrogen atoms of benzene are, therefore, equal, and, as two pairs of hydrogen atoms, symmetrically arranged with reference to one hydrogen atom, are present in benzene, a disubstitution product of benzene cannot occur in more than three isomeric forms.

Basis of the Determination of Position of the Benzene Substitution Products.—The equal value of the six hydrogen atoms

of benzene finds expression in the hexagon formula proposed for benzene.

6 (F C, 6) 2 5 (P C, 6) 3 In showing this the mutual linkage of carbon atoms in the benzene ring can remain in the background. It is very obvious that every diderivative, C₆H₄X₄, resulting from the replacement of two hydrogen atoms can exist in three distinct modifications. Their isomerism is dependent upon the relative position of the two groups entering the benzene. This kind of isomerism is designated isomerism of position or place (1, 43).

In fact, three modifications are known of most of the diderivatives. In no instance are more than three known. Thus there are three

C ₆ H ₄ <oh Dioxybenzenes</oh 	C ₆ H ₄ <\brace{\text{Br}}{\text{NO}_2} Bromnitrobenzenes	$C_6H_4 < \frac{NH_2}{NH_2}$ Diamidobenzenes	$C_6H_4 < OH \\ NO_2$ Nitrophenols.
C ₆ H ₄ <co<sub>2H Oxybenzoic Acids</co<sub>	$C_6H_4 < \frac{CH_3}{CH_3}$ Dimethyl Benzenes	C ₈ H ₄ <co<sub>2H CH₃ Toluic Acids</co<sub>	C ₈ H ₄ CO ₂ H CO ₂ H Phthalic Acids, etc.

The three modifications of each of these compounds may be transformed into the corresponding modifications of the other. Hence, if the relative position of the substituting atoms or atomic groups of the three modifications of one of these bodies has been determined, it is then known for all the others, which can be converted into the three modifications of the first body by easy reactions, unaccompanied by intramolecular atomic rearrangements.

It has been possible to ascertain the opposing position of the substituting groups,—e. g., for the three dibrombenzenes, the three diamidobenzenes, and for the three phthalic acids,—and thus a basis has been obtained for the arrangement of the other disubstitution products into three series, which have been distinguished as the ortho-, meta-, and paraseries.

In the ortho-compounds two adjacent hydrogen atoms of benzene have been replaced. Indicating the six hydrogen atoms with numbers or letters, and arbitrarily making any one of them 1 or a, it will be obvious that two ortho-positions are present: a, b = a, f or 1, 2 = 1, 6 b (2) and f (6) are symmetrical with reference to a (1). The meta-bodies result from the substitution of the hydrogen atoms a, c = a, e or 1, 3 = 1, 5. The positions c (3) and e (5) are symmetrical to a (1). The para-compounds arise from the substitution of the hydrogen atoms a, d or 1, 4. The ortho- and meta-places have two positions of equal value, 5 and 6, also 3 and 5, while the para-position has only 4 to 1.

The position of the substituting groups in diderivatives is indicated by the prefixes ortho-, meta-, and para- before the names of the compounds. These are usually abbreviated to o-, m-, p-, or to numbers included in brackets and placed before the names: [1,2]-, [1,3]-, [1,5]-. The formula is usually written so that an hexagon expresses the benzene ring, and the combined atoms or atomic groups are attached to the six angles of the hexagon.*

^{*} Dr. Siegfried Pfaff has suggested a simpler method of writing. He replaces the

Or, by inserting the designation of position in the ordinary formulas between the benzene residue and the substituting groups—e. g.

The following substances may also be mentioned as chief representatives of the three isomeric series:

	Ortho, [1,2].	Meta, [1,3].	Para, [1,4.]
C'H' <oh< td=""><td>Salicylic Acid.</td><td>Metaoxybenzoic Acid.</td><td>Paraoxybenzoic Acid.</td></oh<>	Salicylic Acid.	Metaoxybenzoic Acid.	Paraoxybenzoic Acid.
$C_{H} < CH_{\bullet}$	Orthoxylene.	Isoxylene.	Paraxylene.
$C_{\bullet}H_{\bullet} < CO_{\bullet}H$	Phthalic Acid.	Isophthalic Acid.	Terephthalic Acid.

Determination of the Positions in Diderivatives.—Dismissing for the moment the mutual linkage of the six carbon atoms, the benzene hexagon permits of the prediction of two chemically identical ortho-, two meta-, and one para-derivatives. The constitution of the three phthalic acids or benzene dicarboxylic acids is evident from the following facts (B. 4, 501):

The phthalic acid resulting from the oxidation of naphthalene is the [1, 2], or orthobenzene dicarboxylic acid. Naphthalene consists of two benzene nuclei, which have in

common two C-atoms holding the ortho-position.

The oxidation of nitronaphthalene produces nitro-o-phthalic acid, which can be changed to phthalic acid. o-Phthalic acid results from the oxidation of amidonaphthalene, formed from nitronaphthalene. This is because the oxidation at one time destroys the one and then the other side of the naphthalene molecule. It shows, further, the constitution of naphthalene, and, again, the constitution of phthalic acid as the o-dicarboxylic acid of benzene:

hexagon by a horizontal line and then distributes the six atoms or atomic groups in the following manner:

$$NO_2 \frac{NO_2}{H} \frac{H}{H} H$$
, $NH_2 \frac{H}{H} \frac{H}{H} N = N \frac{H}{H} \frac{H}{H} H$
o-Dinitrobenzene p-Amidoazobenzene.

Isophthalic acid is benzene-m-dicarboxylic acid, as it can be obtained by the oxidation of isoxylene. The latter is m-dimethylbenzene. This is proved by its formation from mesitylenic acid, the first oxidation product of mesitylene, the [1,3,5] trimethylbenzene:

Ladenburg demonstrated that mesitylene was really [1,3,5]-trimethylbenzene, in that he proved the three non-substituted hydrogen atoms of the mesitylene to be of equal value (A. 179, 174):

The course of the proof is evident from the preceding diagram. Mesitylene yields dinitromesitylene, the NO₂ group of which may replace the hydrogen atoms a and b. From it we get nitroamido-, nitroacetamido-, dinitroacetamido-, dinitroamido-, and dinitromesitylene, identical with the starting-out substance; consequently b and c are of equal value. Nitroamidomesitylene, in which it is assumed that the NH₂ group occupies the position b, yields mononitro-, monoamido-, monoacetamido-, monoacetamido-nitro-, monoamidonitromesitylene, identical with the first nitroamidomesitylene obtained by reduction of dinitromesitylene; hence a and b, or a and c, are of equal value, but, as b and c are considered as of equal value, the equivalence of the three nonsubstituted hydrogen atoms of mesitylene is proved. Mesitylene is symmetrical, therefore the three methyl groups in it must occupy the position [1, 3, 5].

The position [1-4] is all that remains for the third benzene dicarboxylic acid, terephthalic acid. This can be proved in the following manner: Terephthalic acid is obtained from p-dimethyl benzene, and the latter from p-bromtoluene (by means of methyl iodide and sodium). By oxidation p-bromtoluene yields p-brombenzoic acid. p-Brombenzoic acid and p-oxybenzoic acid belong in the same series, as p-oxybenzoic acid can be made from the same p-amidobenzoic acid, by means of the diazo-compound, from which p-brombenzoic acid can be prepared. But it was shown in the preceding paragraphs, in regard to p-oxybenzoic acid (p. 34) that its hydroxyl group replaced an

hydrogen atom which was not arranged symmetrically with reference to any other hydrogen atom in benzene.

The three phthalic acids bear a genetic relationship to the diderivatives of benzene, which do not contain carbon-containing radicals as substituents. The three dinitrobenzenes can be changed to nitroamido-, bromnitro-, bromamido-, and dibrombenzenes on the one hand, and, upon the other, into nitrocyan-, nitrocarboxyl-, amidocarboxyl-, cyancarboxyl-, and phthalic acids by reactions, in which intramolecular atomic rearrangements have not been observed (B. 18, 1492, 1496):

$$\begin{array}{c} C_4H_4 < \stackrel{NO_2}{NO_2} \longrightarrow C_4H_4 < \stackrel{NO_2}{NH_3} \longrightarrow C_4H_4 < \stackrel{NO_2}{Br} \longrightarrow C_4H_4 < \stackrel{NH_2}{Br} \longrightarrow C_4H_4 < \stackrel{NH_2}{Br} \longrightarrow C_4H_4 < \stackrel{NH_2}{CO_2H} \longrightarrow C_4H_4 < \stackrel{CO_2}{CO_2H} \longrightarrow C_4H_4 \longrightarrow C_4H_4$$

W. Körner, in 1874 (Gazz. chim. ital. 4, 305), proved the position of the substituents in the three dibrombenzenes in an entirely different way. This was also done for the three diamidobenzenes in 1872 by P. Griess (B. 5, 192; 7, 1223). The results are concordant among themselves, and agree with that obtained in previous demonstrations. Körner showed that by converting the three known dibrombenzenes into tribrombenzenes the first dibrombenzene would furnish two dibrombenzenes, the second three different tribrombenzenes, and the third but one tribrombenzene. Proceeding from the benzene hexagon, Körner concluded that the first dibrombenzene contained its bromine atoms in the ortho-position, the second in the meta-, and the third in the para-positions. This view is plainly seen in the subjoined diagram. The hydrogen atoms are omitted for the sake of clearness:

The reverse of this proof, if it may be so styled, is found in the idea which P. Griess carried out experimentally.

There are six isomeric diamidobenzoic acids. The diamidobenzene which results from two of these acids by the exit of carbon dioxide is the o-compound, that one which is formed from three of the acids is the m-body, and the product from the sixth acid is the para-derivative:

$$\begin{array}{c|c}
NH_{2} & NH_{2} & NH_{2} & NH_{3} & NH_{4} & NH_{4} & NH_{5} & NH_{5} \\
\hline
NH_{2} & O_{2}H & NH_{2} & O_{3}H & NH_{4} & O_{4}H & NH_{5} & O_{5}H \\
\hline
NH_{3} & NH_{4} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{4} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} \\
\hline
NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5} & NH_{5$$

Further evidence is found in the derivatives of the three isomeric xylenes, thus:

Metaxylene yields 3 nitroxylenes, xylidines, and xylenols, Orthoxylene yields 2 nitroxylenes, xylidines, and xylenols, Paraxylene yields I nitroxylene.

from which it may be concluded that meta- or isoxylene and isophthalic acid have the position [1,3], orthoxylene and phthalic acid the position [1,2], and paraxylene and

terephthalic acid the position [1,4] (B. 18, 2687).

That two adjacent carbon atoms of the benzene nucleus do indeed carry the sidegroups in the ortho-compounds is further obvious from their ability to enter simple reactions, in which, by union of the side-chains, there result carbo- and, particularly, heterocyclic condensation products (compare o-phenylenediamine, o-amidophenol, o-amidothiophenol, o-amidobenzaldehyde, o-phthalic acid, o-oxycinnamic acid, etc.).

There are also crystallographic grounds favoring the idea that the meta-compounds stand between those of the ortho- and para-series (Zeitschrift f. Kryst., 1879, 171; B.

18, R. 148).

The benzene hexagon not only expresses all the relations of isomerism of the benzene derivatives, but also abundantly illustrates their chemical and physical deportment.

Isomerism of the Benzene Polysubstitution Products.— If three or more hydrogen atoms of benzene be replaced, two cases arise: the substituting groups are like or unlike. In the first instance three isomerides of the tri-derivatives—e. g., C₆H₈(CH₈)₈—are possible, and they occupy the positions:

We call them adjacent (1, 2, 3) or (v) = vicinal, unsymmetrical (1, 2, 4) or (as) = asymmetrical, and symmetrical (1, 3, 5) or (s) triderivatives.

Three isomeric structural cases exist likewise for the tetra-derivatives, with four similar groups, CaH2X4 (analogous to the di-derivatives):

Only one modification is possible when there are five and six similar groups; thus

there exists but one pentachlorbenzene, C₆HCl₅, and but one hexachloride, C₆Cl₆.

When the substituting groups are unlike, the number of possible isomerides is far greater; they can easily be derived from the hexagon scheme. Thus, six isomeric modifications correspond to the formula of dinitrobenzoic acid, $C_6H_9(NO_2)_2$. CO_2H :

$$(1, 2, 3)$$
 $(1, 2, 4)$ $(1, 2, 5)$ $(1, 2, 6)$ $(1, 3, 4)$ $(1, 3, 5);$

here the carboxyl group occupies position I.

The constitution of the polysubstitution products of benzene is deduced from their genetic relations to the diderivatives of benzene of known constitution.

See v. Meyer, B. 29, 2564, etc., upon the deportment of polyalkylic benzene derivatives when the acetyl group is introduced by means of acetyl chloride and aluminium chloride, as well as for the conclusions to be drawn from the same in regard to the position of the substituents.

CONSTITUTION OF THE BENZENE NUCLEUS.

In Kekule's formula, proposed in 1865, the six carbon atoms are attached to one another by alternating single and double bonds, forming a closed ring (p. 30). This assumption gives a rather comprehensive view of the entire behavior of the benzene derivatives:

I. It illustrates in the clearest manner possible the methods which have been employed in the synthesis of benzene derivatives (p. 41), benzene condensations, naphthalene, phenanthrene, etc. This has all been verified by the most recent syntheses (that of a naphthol from phenylisocrotonic acid, etc.). Compare also B. 24, 3117.

2. It is in complete harmony with the decomposition reactions of the benzene

nucleus (p. 44).

3. It gives a simple explanation of the fact that only ortho-derivatives (because their side-chains are adjacent) are capable of forming anhydrides, and explains many derivatives due to ortho-condensations. The accepted benzene formula is made quite evident from the manner in which the quinoline ring is formed (Marckwald, A. 280, 1).

4. The assumption of three double unions offers the simplest explanation (without new theories) for the power of benzene derivatives to yield additive products (p. 18). True, this addition does not occur as readily with the normal benzene compounds as it does with the methane compounds, in which there exist ethylene unions; however, aliphatic olefine derivatives also show gradual differences in this particular (see allyl alcohol, I, p. 130). Consult v. Baeyer, A. 269, 181, upon the assumption of para-additions in benzene.

5. Various physical properties argue for the presence of double unions, like those of ethylene, in benzene. Thus, the specific refractive powers indicate the presence of three ethylene unions, CH=CH, in benzene compounds, and five in naphthalene (Brühl, B. 27, 1065). Compare Nasini, B. 23, R. 276. The specific volumes of the benzene derivatives appear to support the idea of three double unions (I, p. 60).

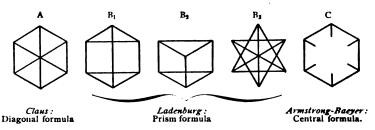
Kekulé's formula for benzene does not fully express the entire symmetry of the benzene nucleus. It would make the ortho derivatives (1, 2) and (1, 6) different, and allow of four different diderivatives, unless we admit Kekulé's idea of the oscillations of the

adjacent carbon atoms (A. 162, 86; B. 5, 463; A. 279, 195).

Perhaps in the formation of an ortho-diderivative there is a displacement of the double union if the substituting groups attach themselves to two singly-linked carbon atoms of the ring, so that that derivative will always be produced in which the substituting groups are joined to doubly-linked carbon atoms. The easier, more complete oxidation of the odiderivatives, as compared with the corresponding m- and p-diderivatives, harmonizes with this conception.

It cannot be denied that the insufficiency of the Kekulé benzene formula is observable when predicting the existence of two instead of one modification of an ortho-disubstitution product. It may also be remarked that the many analogies predominating between the ortho- and meta-derivatives, as compared with the para-bodies, are not fully expressed by this formula. However, this formula, of all benzene formulas, is given the preference in this book, because it allows of a most complete view of the aromatic and aliphatic compounds.

Attention is also directed to other benzene formulas: The diagonal formula of Claus (A), the prism formula of Ladenburg (B₁, B₂, B₃), and the central formula of Armstrong and v. Baeyer (C):



Formulas A and B do not regard double unions as being present in the normal benzene nucleus. The existence of nine single linkages was thought to have been definitely

proved by the specific volumes of the benzene compounds, and especially by their heats of combustion (Theorie der Bildungswärme von J. Thomsen, B. 13, 1808; 14, 2944). According to the most recent researches, the specific volumes argue strongly for the presence of three divalent unions in the benzene nucleus, while the conclusions drawn from the heat of combustion are, in the opinion of Brühl, unfounded (J. pr. Chemie [2], 49, 201).

Ladenburg's prism formula fully accounts for all the static relations of benzene, and explains its isomeric derivatives. It, however, ignores all the double unions, which are proved by the partially reduced benzene nuclei of the di- and tetra-hydro-additive products. It establishes a spacial orientation of the four affinities of the carbon atoms, which is without analogy in the paraffin series, and, in the opinion of its author, leaves to the formula of Kekulé the first place in explaining the various modes of for-

mation and the decompositions of the benzene compounds (B. 23, 1010).

The diagonal formula of A. Claus, with its hexagonal ring and its diagonal or central linkages, explains all the isomeric relations of the derivatives of benzene fully as well as the hexagon formula. It has the advantage that it permits of the formation of either para- or ortho-additive products, because it grants the double carbon-linkages in both the di- and tetra-hydro-benzenes (B. 20, 1422; J. pr. Ch. [2], 49, 505). But it also presents an orientation of the four carbon affinities that is without analogy, and introduces a peculiar central valence, differing from that of the two ring valences.

Baeyer has very recently introduced a central formula, which is very similar to the diagonal formula, but, unlike the latter, does not admit the presence of central linkages. It does not attempt to account for the state or condition of the fourth valence of carbon, but maintains merely that it exerts a pressure directed toward the center. It thus reverts to the hexagonal formula of benzene (Kekulé), which makes no attempt to explain the manner in which the fourth valences are combined (B. 23, 1272; 24, 2689; A. 269,

145; B. 24, R. 728).

Certain constitutional formulas proposed for benzene—e. g., the octahedral formula of Thomsen (B. 19, 2944) and the very noteworthy benzene model of Sacchse (B. 21, 2530; Z. f. phys. Ch. 11, 214; 23, 2062)—are based on stereo-chemical considerations.

The Ch. Ztg. (1894) 18, 155, contains a list of benzene formulas.

BENZENE RING-FORMATIONS.

The nucleus-synthetic reactions of aliphatic bodies, in which the benzene ring is produced, are not especially numerous, but they are, however, very important, because they connect the aliphatic with the aromatic derivatives containing one nucleus. On this account they will be brought together before the individual classes of compounds are discussed, and will be arranged in the order according to which the starting-out bodies under the aliphatic compounds have been discussed:

1. CH4, Methane, conducted through a tube heated to redness, yields benzene.

2. 3CH≡CH, Acetylene, polymerizes at a red heat to bensene (1, p. 96). 3a. 3CH≡C. CH₈, Allylene, is polymerized by concentrated sulphuric acid to [1,3,5]-trimethylbenzene or mesitylene (1, p. 98).

3b. 3CH_a. C\(\equiv \text{C}\). CH_a, Crotonylene, polymerizes to hexamethylbenzene.
4. CCl_a, Perchlormethane, and CCl₂\(\equiv \text{CCl}_1\), perchlorethylene, yield perchlorbenzene when they are conducted through a tube heated to redness; compare perbrombenzene.

5. 3CH=CBr, Monobromacetylene, polymerizes to [1,3,5]-tribrom-

benzene (1, p. 106).

6. C.Hul, Hexyl iodide, when acted upon by iodine chloride, yields hexachlordensene; with bromine the product is hexabrombenzene.

確於ご記 ME LIN F DEMANDON

AND TO The Denzele Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the Compound But a few and a second of the

The second of th

The property of the control of the c

E TELLS IN THE INTERPOLATION OF T

EXCREMINATION OF THE

MEL TEXT III

THE SET

TOTAL

Transier

7

97 semen **Sro**m **2.** - 1 - - 5

F . F . M . :

43

acia t 18 nent

de-

dennes, ark-

> *ition* per-

hree
of
cetylene
er to

natic itain

> xide llow-

other opylid to

ropylaction times

[1,3,5]-

the oxylensations

ensation of and durod (20). densation of

icated in the nenzene ring unds, beari

7a. (CH₂), CH. CH₂. CH: CH. C(CH₃): CH. CHO, Geranial, of citral, yields [1,4]-isopropylloluene or cymene, when it is acted upon with potassium bisulphate.

7b. CH₂. CH₂. CH: C(CH₂). CH: CH. CO. CH₂, from methyl ethyl

acrolein and acetone, yields pseudo-cumene.

7c. (C_3H_7) . CH_2 . $CH: C(C_3H_7)$. CH: CH. CO. CH_3 , from two molecules of isovaleraldehyde and one molecule of acetone, yields di-isopropyltvluene (B. 28, R. 608).

8a. 3CH₃. CO. CH₃, Acetone, under the influence of sulphuric acid,

yields [1,3,5] trimethylbenzene or mesitylene (1, p. 214).

8b. 3CH2. CO. CH2. CH3, Methylethylketone, changes to [1,3,5]-triethylbenzene.

8c. 3CH3. CO. CH2. CH2. CH3. Methyl-n-propylketone, yields [1,3,5]tri-n-propylbenzene.

9. 6CO, Carbon monoxide, combines at high temperatures with potas-

sium to form potassium hexaoxybenzene (1, p. 236).

10. 3CH3. CH2. CH2. COCl, Butyryl chloride, is condensed by Al2Cl4 to triethylphloroglucin.

11. 3CH=C. CO, H, Propiolic acid, polymerizes in sunlight to [1,3,5]

benzenetricarboxylic acid or trimesic acid.

12. 3NO₂CH(CHO)₂, Nitromalonic aldehyde, passes into sym. trinitrobenzene, when its sodium salt is decomposed.

13. NO₂. CH(CHO)₂, Nitromalonic aldehyde, and CH₂. CO. CH₃, ace-

tone, yield p-nitrophenol (B. 28, 2597).

14. 3CH, CO. CH = CH. OH, Oxymethylene acetone, or formyl acetone, condenses very easily to [1,3,5]-triacetylbensene, CoCH3), (I, p. 319).

15a. 2CH₃. CO. CO. CH₃, Diacetyl, is condensed by alkalies to p-

xyloquinone or [2,5]-dimethylquinone.

15b. 2CH₃. CO. CO. CH₂. CH₃, Acetylpropionyl, yields duroquinone

or tetramethylquinone.

- 16. 3CH(OH)=CH. CO₂. C₂H₅, Oxymethylene acetic ester or formylacetic ester, and its dimolecular condensation product, coumalic acid, condense quite readily to esters of [1,3,5]-benzene tricarboxylic acid or trimesic acid.
- 17a. 2CH₃. CO. CO₂H, Pyroracemic acid, and CH₃. CHO, acetaldehyde, when heated with baryta water, condense to [1,3,5]-methylisophthalic acid or uvitic acid.

17b. 2CH3. CO. CO,H, Pyroracemic acid, and CH3. CH2. CHO, pro-

pionic aldehyde, yield [1,3,5]-ethylisophthalic acid.
18. 2CH₃. CO. CHNa. CO₂. C₂H₅, Sodium acetoacetic ester, and CHCl₂, chloroform, rearrange themselves to oxyuvitic ester or oxymethylisophthalic ester.

CH₃. C: CH. CO. CH. CO. CH₃, Dehydracetic acid, yields orcinol or

3,5-dioxytoluene.

20. 2CH₃. CO. CH₂. CO. CO₂. C₂H₅, Acetonoxalic ester, condenses to oxytoluic ester.

It is very doubtful whether a synthesis occurs in the production of *mellitic acid* or benzene hexacarboxylic acid, $C_0(CO_2H)_6$, by the oxidation of coal or graphite. It is more probable that this reaction must be regarded as a transformation or rearrangement of a carbon molecule consisting of twelve carbon atoms.

Reviewing the aliphatic bodies which are converted into benzene derivatives by nucleus-synthetic reactions, it will be discovered that

1. Certain saturated bodies like methane (1) and tetrachlormethane (4) yield the benzene ring under the influence of heat,—by pyrocondensation. Many benzene derivatives, like benzene, the methyl benzenes, the simple amido- and oxybenzenes, are distinguished by their remarkable stability at high temperatures (see coal tar, p. 48).

2. Perchlorbenzene has been observed in the exhaustive chlorination of many aliphatic substances. Hexyl iodide (6) is converted into per-

chlor- and perbrom-benzene with especial ease.

3. A great number of aliphatic acetylene derivatives containing a trebly-linked pair of carbon atoms *polymerize*, and by the union of three similar molecules form benzene derivatives. The polymerization of acetylene to benzene (2) occurs with the greatest difficulty. Bromacetylene (5) polymerizes much more readily. Allylene (3a) and crotonylene (3b) require sulphuric acid, and propiolic acid (11) sunlight in order to bring about *aromatic polymerization*.

The other aliphatic compounds capable of condensing to aromatic substances, which, in other words, manifest aromatic condensation, contain carbon and oxygen linked doubly to each other. Many of them are

ketones; others contain the oxymethylene group.

4. The production of potassium hexaoxybenzene from carbon monoxide and potassium (9) is based upon a direct addition-reaction. The follow-

ing are hydrolytic condensations:

5. The ring-formation in the transition of citral or geranial and other high molecular keto-olefines into cymene, pseudocumene, and isopropyltoluene (7a, b, c), as well as the condensation of dehydracetic acid to orcinol (19). This proceeds with the exit of carbon dioxide.

6. The condensation of acetone, methyl-ethyl- and methyl-n-propylketone to [1,3,5]-trialkylic benzenes (8a, 8b, 8c). A similar reaction is that of butyryl chloride, which splits off hydrochloric acid three times

and condenses to triethylphloroglucin (10).

7. The condensation of pyroracemic acid and aldehydes to [1,3,5]-

alkylic isophthalic acids (17a, 17b).

8. The condensations of nitromalonic aldehyde and of the oxymethylene compounds (12, 13, 14, 16) are related to the condensations considered under 6 and 7.

9. Two aliphatic molecules take part in the hydrolytic condensation of a diketones—e. g., diacetyl and acetylpropionyl to p-xylo- and duroquinone (15a, 15b); (10) acetonoxalic acid to oxytoluic acid (20).

11. Three aliphatic molecules (18) participate in the condensation of

chloroform and sodium acetoacetic ester.

Various other reactions attach themselves to those indicated in the preceding paragraphs, which lead to the formation of the benzene ring. They result in the production of hydroaromatic compounds, bearing

an intimate kinship to the derivatives of benzene. Some of them are:

- 1. Sodium malonic ester condenses to phloroglucin tricarboxylic ester, sodium acetone dicarboxylic ester to dioxyphenylaceto-dicarboxylic ester, while triketohexamethylene dicarboxylic ester is formed from acetone dicarboxylic ester and malonic ester (B. 29, R. 1117). All these condensation products are probably hexahydrobenzene derivatives.
- 2. Succinic ester is condensed by metallic sodium to succinylosuccinic ester.
- 3. $\alpha\gamma$ -Diacetoglutaric ester changes readily to 3-methyl- Δ_1 -ketohexamethylene. Condensations of δ -diketo bodies, such as the preceding, are rather numerous. Thus, γ -acetobutyric ester, CH₁. CO. CH₂. CH₁.-CH₁. COOC₂H₅, and sodium ethylate yield dihydroresorcinol, which conversely breaks down into γ -acetobutyric acid (compare decompositions of the benzene ring).

Other methods showing the synthesis of hydroaromatic compounds

have already been given (pp. 20, 21).

DECOMPOSITIONS OF THE BENZENE RING.

The benzene derivatives in general are characterized by the stability of the benzene ring. To break the latter down the proper benzene bodies are acted upon by reagents which open up the double union in part or entirely. Hence, the decomposition is invariably preceded by the formation of hydroaromatic intermediate products, which usually cannot be isolated. Often decomposition products result, which still contain the six carbon atoms in the molecule as an open chain, but usually they are fragments of the decomposition, and in some instances they are pentacarbocyclic derivatives formed from hexacarbocyclic a-diketones.

The phenols, amidophenols, quinones, oxyquinones, and phenol car-

boxylic acids are most suitable for the ring decomposition.

1. Decomposition by Moderated Oxidation.—Although energetic oxidation decomposes the benzene nucleus of the aromatic substances referred to in such a manner that bodies containing two carbon atoms result,—e. g., carbon dioxide, formic acid, and oxalic acid,—yet it has been possible, by means of nitrous acid, to oxidize pyrocatechol or [1,2]-dioxybenzene, C_eH₄[1,2](OH)₂, and protocatechuic acid or [3,4]-dioxybenzoic acid, CO₂H[1]C₆H₃[3,4](OH)₂, to dioxytartaric acid (Kekulé).

Phenol, C₄H₅OH, has been converted by dilute potassium perman-

ganate into mesotartaric acid (Döbner).

2. Decomposition by Simultaneous Chlorination and Oxidation.—When benzene is treated with potassium chlorate and sulphuric acid, trichlorphenomalic acid or β -trichloracetoacrylic acid (1, p. 382) is produced (chlorquinone is an intermediate product), which breaks down, under the influence of baryta water, into chloroform and maleïc acid (Kekulé and Strecker):

Potassium chlorate and hydrochloric acid change phenol, salicylic acid, or o-oxybenzoic acid, $\text{CO}_2\text{H[1]C}_6\text{H}_4\text{[2]OH}$, and gallic acid, $\text{CO}_2\text{H[1]C}_6\text{H}_2\text{[2,3,4](OH)}_3$, into trichlorpyroracemic acid or isotrichlorglyceric acid, $\text{CCl}_3\text{C}(\text{OH})_2\text{CO}_2\text{H}$ (see 1, 370).

Bleaching lime converts picric acid or [10H,2,4,6]-trinitrophenol into chlorpicrin (vol. 1), while bromine and lime-water change it to brompicrin (vol. 1).

Zincke has given an interesting method for the decomposition of the benzene nucleus. It consists in preparing chlorinated R hexene- and R-hexylene ketones from suitable aromatic bodies, and then decomposing the first.

Four examples may be given. The first three attach themselves to the three dioxybenzenes and the fourth to [1,3,5]-trioxybenzene or phloroglucin.

1. Chlorine converts pyrocatechol or o-dioxybenzene first into tetrachlororthoquinone, and this into hexachlor-o-diketo-R-hexene. The latter compound, when digested with water, sustains a rearrangement into hexachlor-R penteneoxycarboxylic acid, which chromic acid oxidizes to hexachlorketo-R-pentene. Caustic soda resolves the R-pentene ketone into perchlorvinylacrylic acid, which becomes ethidenepropionic acid upon reduction (B. 27, 3364):

2. The decomposition of hydroquinone proceeds more simply. Tetrachlorparaquinone is readily formed by the action of chlorine upon hydroquinone or quinone, as well as by the action of potassium chlorate and hydrochloric acid upon phenol. The further addition of chlorine leads to hexachlorparadiketo-R-hexene, which is converted by alcoholic potash into perchloracroylacrylic acid. The latter, and also hexachlorparadiketo-R-hexene itself, are decomposed by aqueous caustic soda into dichlormaleïc acid, trichlorethylene, and hydrochloric acid (A. 267, 1):

3. Chlorine converts resorcinol, in glacial acetic solution, into pentachlorresorcinol, and this into heptachlorresorcinol. Both m-diketochlorides are decomposed by cold water; the pentachlor-derivative yields dichloracetotrichlorcrotonic acid, while the hepta-body yields trichloracetopentachlorbutyric acid under the influence of chlorine and water. When dichloracetotrichlorcrotonic acid is boiled with water it becomes dichlormethylchlorvinyl o-diketone. Trichloracetopentachlorbutyric acid is decomposed by alkalies, the same as trichloracetoacrylic acid, into chloroform and pentachlorglutaric acid. If, however, it be treated with boiling water, it changes to tetrachlordiketo-R-pentene, which chlorine converts into the chloride of perchloracetoacrylic acid. Water changes the chloride to the acid, which alkalies decompose into chloroform and dichlormaletic acid:

4. Phloroglucin, or [1,3,5] trioxybenzene, behaves just like resorcinol. Chlorine converts it into hexachlor-[1,3,5] triketo-R-hexylene. Water and chlorine decompose the triketone into octochloracetylacetone; methyl alcohol changes it to the dimethyl ester of dichlormalonic acid, and sym. tetrachloracetone; while with ammonia it yields three molecules of dichloracetamide (B. 23, 1706):

In the four preceding examples the decomposition occurs between a CO-group and a CCl₂-group of a ketochloride. Zincke first elaborated these reactions in the naphthalene series, and used them to effect the decomposition of the one naphthalene nucleus, and for the transformation of naphthalene into indene derivatives. Later he extended them

to the phenols and other aromatic bodies which have been mentioned. Hantzsch, in like manner, effected the decomposition of phenol in an alkaline solution, and changed it to cyclopentene compounds (B. 22, 1238).

3. Decomposition by Reduction in Alkaline Solution.—This decomposition is shown by—

I. The o-phenolcarboxylic acids when they are reduced by metallic sodium in amyl alcoholic solution. It is very probable that the intermediate products of the reduction are tetrahydroacids and their products of rearrangement—the hydroaromatic o-ketone carboxylic acids. The latter absorb water and become pimelic acids. Salicylic acid is converted almost quantitatively into n-pimelic acid, while o-, m-, and p-cresotinic acids yield the three isomeric methyl pimelic acids (Einhorn and Willstätter, B. 28, R. 744):

This reaction has been carried out with equal success with the naphthalene-o-oxycarboxylic acids (see decompositions of the naphthalene ring).

II. Reduction changes resorcinol into dihydroresorcinol, which is converted into n-glutaric acid by oxidation with potassium permanganate (Merling, A. 278, 32). If dihydroresorcinol be heated for several hours with a concentrated baryta solution to 150–160°, it takes up water and decomposes into γ -acetobutyric acid (Vorländer, B. 28, 2348):

This reaction can be made retrogressive (compare p. 44).

I. BENZENE HYDROCARBONS CONTAINING A SINGLE NUCLEUS.

Benzene, Phene, C₆H₆, melting at + 5.4° and boiling at 80.4° (760 mm.), is the parent hydrocarbon of the aromatic compounds. It is produced in the dry distillation of coal, and is accordingly present in coal tar, accompanied by thiophene, C₆H₆S (a body which may be readily confounded with it in physical properties), and numerous other deriva-

tives. Pure benzene is obtained by heating benzoic acid or other benzene polycarboxylic acids with lime. It is prepared synthetically by heating acetylene to high temperatures (Berthelot, 1870).

Benzene is obtained from coal tar by fractional distillation. The presence of thiophene in it is readily determined by the indophenine or phenanthraquinone reaction (see The thiophene can be removed from the benzene by shaking the latter with concentrated sulphuric acid, or by acting upon it with aluminium chloride (B. 29, R. 1000, 1152). It is finally purified by surrounding it with a freezing mixture, and the crystalline benzene is pressed out in the cold.

History (B. 23, 1271).—Faraday (1825) discovered benzene in an oil obtained by the compression of illuminating gas. In 1834 Mitscherlich obtained it by distilling benzoic acid with lime, and in 1845 Hofmann found it in coal tar.

Properties.—Benzene is a mobile, ethereal-smelling liquid, of specific gravity 0.899 at 0° (0.8799 at 20°). It burns with a luminous flame, mixes with absolute alcohol and ether, and readily dissolves resins, fats, and many carbon compounds, some of which crystallize out in combination with the benzene (see triphenylmethane). Sulphur, iodine, and phosphorus are also soluble in benzene.

Deportment and Transformations.—(1) When benzene is conducted through tubes heated to redness it loses hydrogen and changes partly into diphenyl, C_8H_5 , C_6H_6 , diphenyl benzenes, C_8H_4 (C_6H_5)₂, etc., and in part into acetylene. (2) If benzene be acted upon with manganese dioxide and sulphuric acid some benzoic acid is produced, due evidently to the diphenyl formed at first (A. 221, 234), and also o-phthalic acid. The benzene is, however, quite stable in the presence of oxidants; but when potassium chlorate and sulphuric acid act upon it, it is torn asunder and becomes trichlorphenomalic acid or β -trichloracetoacrylic acid (p. 45). Benzene exposed for a long period to the action of ozone changes to a white, amorphous mass—ozohenzene. This is a very explosive body. It has the formula $C_6H_6O_6$. Water slowly decomposes it (B. 28, R. 540, 1054). (3) Hydriodic acid reduces it to [cyclohexane] or hexahydrobenzene (see this) (A. 278, 88). (4) Chlorine and bromine not only add themselves to benzene, but also reduced the control of the place its hydrogen (p. 58). (5) Nitric acid converts it into nitrobenzene, C₄H₆NO₂. (6) Sulphuric acid changes it to benzene sulphonic acid, C₆H₅SO₃H. These last two compounds are made upon a technical scale. Alkyl residues can be introduced into benzene by the action of Al₂Cl₆ and alkylogens (see formation (4) of benzene hydrocarbons, p. 50). (7) Benzene and aldehydes are condensed by sulphuric acid to higher aromatic hydrocarbons (see diphenylmethane and diphenylethane).

COAL TAR.

Not only benzene, but also numerous methyl benzenes and many more highly condensed aromatic hydrocarbons, like naphthalene, C₁₀H₆, acenaphthene, $C_{12}H_{10}$, fluorene, $C_{13}H_{10}$, anthracene and phenanthrene, $C_{14}H_{10}$, fluoranthene, $C_{15}H_{10}$, pyrene, $C_{16}H_{10}$, chrysene, $C_{18}H_{12}$, etc., are obtained by the dry distillation of coal. They are present in coal tar, which is produced in great quantities in the manufacture of illuminating gas and in the coke industry. In addition to gas and tar, which are products of coal distillation, mention must also be made of the ammonia water. These are the volatile products. Coke remains in the retorts. It is a better fuel than coal; it is richer in carbon.

The rapid, brilliant development of the chemistry of the benzene de-

rivatives is largely due to the fact that the aromatic parent hydrocarbons are so largely present in coal tar, and are accessible in large amounts through various technical industries. The very nature of the paraffins renders them unsuitable for the preparation of the aliphatic bodies, whereas the benzene hydrocarbons, because of the readiness with which they enter into all kinds of reactions, constitute not only the systematic, but also the practical foundation for the upbuilding of the chemistry of the aromatic derivatives. Coal tar, which contains these hydrocarbons, is an inexhaustible source for the preparation of numerous benzene derivatives, not a few of which have found extensive application as dyes or medicines.

The Working of Coal Tar for Aromatic Hydrocarbons.—The tar contains not only aromatic hydrocarbons, but also paraffins, thiophene, methylated thiophenes, phenols, pyridine bases, and other derivatives. It is first distilled and then separated into three or four fractions:

- 1. Light Oil (3-5 per cent.), specifically lighter than water and boiling up to 150°.
- 2. Middle Oil (8-10 per cent.), having about the same specific gravity as water and boiling from 150-210°.
- 3. Heavy Oil (8-10 per cent.), heavier than water and boiling at 210-270°.
- 4. Green Oil or Anthracene Oil (16-20 per cent.), colored green, and boiling from 270-400°.
- 5. Residue: pitch.

It is only the light oil which is of value when the aromatic hydrocarbons are under consideration. It is freed from resins, olefines, pyridine bases, etc., by washing with sulphuric acid, and from phenols by treating it with caustic soda. After this it is subjected to careful, fractional distillation in a column apparatus like that employed in the purification of alcohol (1, p. 123).

Besides benzene, coal tar contains toluene or methyl benzene, the three isomeric xylenes or dimethyl benzenes, ethyl benzene, vinyl benzene or styrene, the three isomeric trimethyl benzenes; mesitylene, pseudocumene, hemimellithene and durene or tetramethyl benzene. Aromatic hydrocarbons also occur abundantly in the tar from peat, in small amount in the tar from wood, in that from bituminous shales, and in petroleum.

To properly understand the formation of the aromatic hydrocarbons by the dry distillation of coal we should take into consideration that they are produced with hydrogen evolution on passing simple, fatty bodies like methane, alcohol, ether, etc., through tubes heated to redness (B. 29, 2691). Such reactions are termed pyrogenic syntheses or pyrocondensations, in which acetylene and allylene particularly play an important rôle. Just as acetylene yields benzene, so acetylene and allylene form toluene, and benzene and acetylene yield naphthalene, etc. (A. 139, 281; B. 10, 853; 11, 1213; 18, 3032; 19, 2513; 20, 660). The glowing sides of the retort with which the volatile products resulting in the heating of coal come in contact give every opportunity for such pyrocondensations. However, the nature of the starting-substances should really be carefully considered (B. 28, 488).

ALKYL BENZENES, CaHza-e.

The nucleus-synthetic reactions (1, 85) stand first among the general methods of formation used in connection with the alkyl benzenes (it has been indicated in preceding paragraphs that the methyl benzenes occur in coal tar).

1. It has been repeatedly stated that various symmetric trialkylic benzenes have been obtained by the polymerization of alkyl acetylenes with sulphuric acid, similarly to the polymerization of acetylene to benzene (p. 41):

Allylene, $3CH_a$. $C \equiv CH \xrightarrow{SO_4H_a} C_4H_a[1,3,5](CH_a)_a$, Mesitylene. Ketones, such as acetone, ethylmethyl ketone, etc., can be treated with sulphuric acid, instead of the alkyl acetylenes (p. 42).

2. The reaction of Fittig, discovered in 1864, is more generally used. It consists of the action of sodium upon a mixture of brominated benzenes, and the bromides or the iodides of the alkyls in ethereal solution (A. 129, 369; 131, 303; B. 21, 3185):

This reaction is a valuable generalization of the synthesis applied by Würtz to the paraffins, which consisted in acting on the alkylogens with sodium (1, 84). A few drops of acetic ether sometimes accelerate the reaction, which proceeds the more smoothly the greater the molecular weight of the alkyl iodide.

3. The synthesis of isopropyl benzene from benzal chloride and zinc methide (B. 13, 45), and that of the one amyl benzene from benzal chloride and zinc ethide, corresponds to that of tetramethyl methane from acetone chloride and zinc methide (1, 85);

$$C_6H_5CHCl_2 + Zn(C_2H_5)_2 = C_8H_5CH(C_2H_5)_2 + ZnCl_2.$$

4. The so-called aluminium chloride synthesis discovered by Friedel and Crafts in 1877, although restricted to the aromatic series, is there very generally applicable. It consists in the action of alkylogens upon benzene hydrocarbons in the presence of aluminium chloride.

Zinc chloride and ferric chloride act similarly. It is very probable that metalloorganic bodies— e,g,C_6H_5 . Al₂Cl₅—are formed at first. These then react with the alkylogens. No difficulty is experienced in replacing all the hydrogen atoms of benzene by methyl or ethyl groups (B. 14, 2624; 16, 1745). Sometimes carbon disulphide acts favorably as a diluent (A. 235, 207; B. 29, 2884):

$$\begin{split} & \text{CH}_3\text{Cl} + \text{C}_6\text{H}_6 & \xrightarrow{\text{Al}_2\text{Cl}_6} & \text{HCl} + \text{C}_6\text{H}_5\text{CH}_3 \\ & \text{2CH}_3\text{Cl} + \text{C}_6\text{H}_6 - \xrightarrow{\text{Al}_2\text{Cl}_6} & \text{2HCl} + \text{C}_6\text{H}_6(\text{CH}_3)_2 \\ & \text{6CH}_3\text{Cl} + \text{C}_6\text{H}_6 & \xrightarrow{\text{Al}_2\text{Cl}_6} & \text{6HCl} + \text{C}_6(\text{CH}_3)_6. \end{split}$$

Various haloid compounds— ϵ . g., chloroform (see triphenylmethane)—and the acid radicals (see benzophenone and acetophenone) react similarly with benzene.

Decomposition Reactions .- 5. It is rather singular that aluminium chloride lends

itself as well to the breaking-down of alkyl benzenes as to their synthesis.

Thus, aluminium chloride acting alone, or more especially when HCl is conducted into polyalkylic benzenes mixed with aluminium chloride, causes the side-chains to split off in the form of alkyl chlorides (A. 235, 177). Under proper experimental conditions it is possible, with the aid of aluminium chloride, to remove the side-chains from one molecule of an hydrocarbon into another molecule of the same hydrocarbon. In so doing the aluminium chloride seems to prefer certain very definite positions of the alkyl groups both in the synthesis and in the decomposition. This is illustrated in the following diagram (Anschütz and Immendorff, B. 18, 657):

- 6. Concentrated sulphuric acid acts in the same decomposing way, building up new bodies at the same time (see durene, p. 55).
- 7. Dry distillation of a mixture of aromatic acids with lime or sodalime (1, p. 81); iron filings are introduced to accelerate the conduction of heat. All the carboxyl groups are split off in the reaction and the original hydrocarbons set free:

8, 9, and 10. The replacement of inorganic residues in substitution products of the aromatic hydrocarbons by hydrogen.

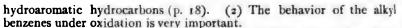
8. Treatment of diazo-bodies with alcohol or an alkaline solution of stannous oxide (B. 22, 587). This reaction is of special value in the determination of questions of constitution. The diazo-bodies are obtained from amido-compounds, and these from nitro-derivatives, which result when nitric acid acts upon the hydrocarbons.

 Treatment of sulpho-acids (see these) with superheated steam and sulphuric acid, concentrated hydrochloric acid or phosphoric acid at 180°.

ro. Heating the oxygen derivatives—e. g., phenols and ketones—with zinc dust (Baeyer, A. 140, 295), or with hydriodic acid and phosphorus. It is remarkable that benzophenone, C₆H₅. CO. C₆H₅, for example, is readily reduced, while the opposite is true of diphenyl ether, C₆H₅. O.-C₆H₅.

Properties.—The hydrocarbons of the benzene series are chiefly volatile liquids; some polymethylbenzenes—durene, penta- and hexamethylbenzene—are solids at ordinary temperatures. They possess a peculiar, not disagreeable odor, and are insoluble in water. They dissolve readily in alcohol and in ether. They are excellent solvents for many organic substances, which can be precipitated from solution by petroleum ether.

Deportment and Transformations.—(1) Reducing agents, particularly hydriodic acid, convert the alkyl benzenes, and also benzene itself, into



Acids are produced (aromatic acids) by oxidizing their side-chains with nitric acid, a chromic acid mixture, potassium permanganate, or

ferricyanide of potassium.

The number and position of the resulting CO₂H groups with reference to each other afford evidence as to the number and position of the alcohol radicals contained in the oxidized hydrocarbon. When long side-chains are carefully oxidized, particularly with potassium permanganate, intermediate products can be obtained, since the oxidation occurs according to the rules which prevail with aliphatic compounds (compare aromatic acids).

(3) Chlorine and bromine replace the hydrogen of the benzene nucleus when they act upon it in the cold, whereas it is the hydrogen of the side-

chains which is substituted in the heat (toluene, pp. 54, 61).

(4) Concentrated nitric acid produces nitro bodies.

- (5) Concentrated sulphuric acid, aided by heat, dissolves the alkyl benzenes with formation of sulphonic acids. The hydrocarbons can be recovered again from the latter (see method 9). This constitutes the basis of a method for the separation of the benzenes from the paraffins, as well as affords a means of obtaining the former in a state of purity.
- (6) Chromyl chloride, CrO, Cl2, unites with the benzene homologues to form compounds which water converts into aromatic aldehydes and ketones (see these).

Isomerism. — Toluene, the first member of the series, is only known in one modification. More are not possible. The six hydrogen atoms of benzene are equal (p. 30).

Xylene, or dimethyl benzene, is a disubstitution product; therefore three

isomerides are possible (p. 32):

o-Xylene,
$$C_6H_4\left\{ \begin{bmatrix} 1\\2\end{bmatrix}CH_3 \\ CH_3 \end{bmatrix}$$
 m-Xylene, $C_6H_4\left\{ \begin{bmatrix} 1\\3\end{bmatrix}CH_3 \\ CH_3 \end{bmatrix}$ p-Xylene, $C_6H_4\left\{ \begin{bmatrix} 1\\4\end{bmatrix}CH_3 \\ CH_3 \end{bmatrix}$

The three xylenes are known. Ethyl benzene, C₄H₅C₂H₅, is isomeric with them.

There are eight possible isomerides of the formula C₂H₁₂; all of them are known. They are-

1. Three trimethyl benzenes. 2. Three ethylmethyl benzenes.

3. Two propyl benzenes: n-propyl and isopropyl benzene.
The phenomena of isomerism are, therefore, influenced by the place or position, the number, the homology and isomerism of the alkyls, which

have entered the benzene as substituents of the hydrogen.

Constitution.—Of all the syntheses of alkyl benzenes, the reaction of Fittig is most suitable for the deduction of conclusions in regard to constitution, because, so far as is known, intramolecular atomic rearrangements do not occur in it—that is, the alkyls assume the position previously held by the halogen atom. Further, the oxidation reaction is important in deciding upon the number and position of the side-chains (see above).

Name.	FORMULA.	М. Р.	B. P.	SPECIFIC GRAVITY
Toluene,	C ₆ H ₅ .CH ₅	_	110.3°	o.8708 (13.1/4°)
Xylenes, Dimethyl Benzenes, .	$C_6H_4(CH_3)_2$		_	
o-Xviene	1	28°	142°	0.8932 (0°)
m-Xylene, Isoxylene,		— 54°	139°	0.8812 (0°)
p-Xylene,		+ 15°	138°	0.8801 (0°)
Ethyl Benzene,	$ C_{\alpha}H_{\alpha}.CH_{\alpha}.CH_{\alpha} $	_	134°	0.8832 (0°)
Trimethyl Benzenes,	C.H.(CH.),			1 ,
[1.2.3] = Hemimellithene.	1		175°	_
[1.2.4]=Pseudocumene.	1		170°	
[1,3,5] = Mesitylene.	1		164.5°	0.8694 (9.8/4°)
[1,3,5] = Mesitylene, Methylethyl Benzenes,	C.H.(CH.)(C.H.)		4.3	
o- or [1.2]	-64(3/(-35/		159°	0.8731 (16°)
o- or [1,2]-,		_	159°	0.8690 (20°)
n- or I Ale			162°	0.8652 (21°)
p- or [1,4]-,	сн сн сн сн		158.5°	
Isopropyl Benzene, Cumene,	CHCHCH		153°	0.8798 (0°)
Tetramethyl Renzene	CH (CH)	_	153	0.0790 (0)
Tetramethyl Benzene, [1,2,3,4]=Prehnitol,	C6112(C113)4 · · ·	.0	204°	
[1,2,3,4]=1 renultoi,		—4°		0 8062 (0/48)
[1,2,3,5]=Isodurene,		0	196°	0.8961 (0/4°)
[1,2,4,5]=Durene,		79°	190°	-
Cymene, [1,4]-Methylisopropyl Benzene,	CH (CH)(CH)			0
pyl Benzene,	$C_6H_4(CH_3)(C_5H_7)$.	_	175°	0.8723 (0°)
Pentamethyl Benzene,	$C_6H(CH_3)_6$.	53°	230°	_
Hexamethyl Benzene,	$C_6(CH_3)_6$	164°	264°	
Pentamethyl Benzene,	$C_6H(C_2H_5)_5$	-	277°	0.8985 (19°)
Hexaethyl Benzene,	$C_6(C_2H_5)_6$	129°	298°	_ ` `

It is apparent from this table that the position isomerides of the same formula—that is, the three xylenes—have almost the same boiling point. In the case of the dimethyl benzenes the o-modification has the highest-boiling point; then follows the meta-body, and finally the p-compound. However, the latter has the highest melting point. Durene of the tetramethyl benzenes is a solid at the ordinary temperature. This is also true of pentamethyl-, hexamethyl-, and hexaethyl-benzenes. The entrance of methyl into the side-chain raises the boiling point about 24°. See toluene, ethyl benzene, and n-propyl benzene.

Toluene, C₆H₅CH₅, so called because it is produced in the dry distillation of tolu balsam, occurs in coal tar, accompanied by thiotolene or methyl thiophene (see this). It is very valuable from a commercial standpoint. It is produced by the usual methods:

1. From brombenzene, methyl iodide, and sodium.

No. of Lorent

- 2. From benzene, methyl chloride, and aluminium chloride.
- 3. From the polymethyl benzenes and aluminium chloride.
- 4. By distillation of the three toluic acids and the methyl polycar-boxylic acids with lime, etc.

Reduction changes toluene to hexahydrotoluene: dilute nitric acid and chromic acid oxidize it to benzoic acid; chromyl chloride, CrO₂Cl₂, and water convert it into benzaldehyde.

It yields o- and p-nitrotoluene upon nitration, and when it is sulphonated much p-toluene sulphonic and little of the o-acid result.

The action of chlorine upon toluene deserves mention. At boiling temperatures it is exclusively the hydrogen of the side-group which is substituted, and the products are:

Benzyl chloride, Benzal chloride, Benzo-trichloride, C₂H₃CHCl₂, Benzo-trichloride, C₃H₃CCl₃.

o- and p-Chlortoluene, C₆H₄Cl. CH₃, are produced in the cold. In the presence of iodine and SbCl₆ the chlorine only enters the nucleus even in the cold (Beilstein and Geitner, A. 139, 311). Phosphorus pentachloride, however, renders the entrance of chlorine into the sidechain more easy (A. 272, 150).

Hydrocarbons, C₈H₁₀.—Ethyl benzene is isomeric with the three dimethyl benzenes. Iso- or m-xylene, of the three xylenes occurring in coal-tar, is present in the largest amount, and is of technical value.

When the mixture is boiled with dilute nitric acid, the ortho- and para- varieties are changed to their corresponding toluic acids, which are finally oxidized to o- and p phthalic acids. Metaxylene is attacked with more difficulty. Potassium permanganate oxidizes the three xylenes to their corresponding toluic acids and these to phthalic acids. On shaking crude xylene with ordinary sulphuric acid, the ortho- and meta-xylene dissolve to form sulphonic acids, which are separated through their salts and sulphamides (B. 10, 1013; 14, 2625). p-Xylene volatilizes first when crude xylene is distilled with steam.

o-Xylene is obtained from brom-toluene by means of CH₃I and sodium. Potassium permanganate oxidizes it to phthalic acid. Chromic acid decomposes it, like many other o-diderivatives, into carbon dioxide and water.

m-Xylene, or Isoxylene.—The production of mesitylene by the distillation of mesitylenic acid with lime is of great theoretical importance. This reaction genetically links m-xylene to mesitylene, in which the [1,3,5]-position of the three methyl groups may be demonstrated. This, then, would also prove the m-position for the toluic acid and phthalic acid resulting from the oxidation of m-xylene (p. 37).

p-Xylene is formed when camphor is distilled with ZnCl₂. It is obtained pure by the action of sodium and CH₃I upon p-bromtoluene and p-dibrombenzene (B. 10, 1355). Dilute nitric acid oxidizes it first to p-toluic acid and subsequently to terephthalic acid Chromic acid converts it immediately into the latter acid. Paraylene is soluble in fuming sulphuric acid only; its sulphonic acid forms large crystals, and is not very soluble.

Ethyl Benzene, C₆H₅. C₂H₅, also present in coal tar, is produced by the action of sodium upon C₆H₅Br and C₂H₅Br, and hydriodic acid upon styrolene, C₆H₅. C₂H₃, but best by the action of C₆H₅Br and AlCl₃ upon benzene (B. 22, 2662). Dilute nitric acid and chromic acid oxidize it to benzoic acid; CrO₂Cl₂ converts it into phenyl acetaldehyde, C₈H₅. CH₂. CHO.

Hydrocarbons, C₉H₁₂.—The isomerism of the eight compounds of this formula has been mentioned (p. 52): three trimethyl benzenes, three

methyl ethyl benzenes, and two propyl benzenes. The physical constants of these eight hydrocarbons are given in the table exhibited on

Mesitylene, symmetrical trimethyl benzene, C_eH_s(CH_s)_s, occurs in coal tar, and is produced by distilling acetone (Kane, 1837) or allylene with concentrated sulphuric acid (p. 42; compare B. 29, 958, 2884).

The proof of its symmetrical structure (p. 37) is of fundamental importance in determining the position of benzene substitution products. Dilute nitric acid converts mesitylene into mesitylenic acid, mesidic acid or uvitic acid, and trimesic acid:

$$C_{\mathbf{e}}H_{\mathbf{s}} \begin{cases} \begin{bmatrix} \mathbf{I} \end{bmatrix} \mathbf{C}H_{\mathbf{s}} \\ 3 \end{bmatrix} \mathbf{C}H_{\mathbf{s}} \longrightarrow C_{\mathbf{e}}H_{\mathbf{s}} \\ \begin{bmatrix} \mathbf{I} \end{bmatrix} \mathbf{C}O_{\mathbf{s}}H \\ 3 \end{bmatrix} \mathbf{C}O_{\mathbf{s}}H \\ \begin{bmatrix} \mathbf{I} \end{bmatrix} \mathbf{C}O_{\mathbf$$

Pseudocumene, [1,3,4]-trimethyl bensene, also occurs in coal tar. It is separated from mesitylene by means of its more difficultly soluble sulpho-acid (B. 9, 258), from which it is subsequently isolated (p. 51). It is formed from brom-p-xylene and 4-brom-m-xylene. This is evident from its constitution.

Hemimellithene, [1,2,3]-trimethyl benzene, occurs in coal tar (B. 19, 2517), and is obtained from isodurylic acid, C₄H₂(CH₃)₃. CO₂H. It may be synthesized by the action of metallic sodium and methyl iodide upon 2-brom-m-xylene.

The three Ethyl Toluenes have been prepared from the three brom-toluenes by The three Ethyl Toluenes have been prepared from the three brom-toluenes by means of ethyl bromide and sodium. The [1,4]-compound from p-brom-toluene, ethyl bromide, and sodium (B. 28, 2648), melts at 162°.

n-Propyl Benzene is obtained from C₈H₈Br, n-propyl iodide or bromide and sodium, or from benzyl chloride, by the action of zinc ethide. It can also be produced from benzene by the action of n-propyl bromide and Al₂Cl₆ at -2° (B. 24, 768).

Isopropyl Benzene, C₈H₅.C₈H₇, called Cumene, was first made by distilling cumic acid with lime. It can be synthesized by the action of AlCl₈ upon a mixture of benzene with isopropyl bromide or chloride, and from benzal chloride. C.H. C.H.Cl., by means of

with isopropyl bromide or chloride, and from benzal chloride, C₆H₅. CHCl₂, by means of zinc methide. As n-propyl bromide is rearranged when warm by Al₂Cl₆ into isopropyl bromide, isopropyl benzene is produced in this synthesis with Al₂Cl₆ if the experiment is not conducted in the cold. In the animal organism isopropyl benzene yields propyl phenol (B. 17, 2551).

Twenty-two isomerides are possible for the hydrocarbons, C₁₀H₁₄:

$$\begin{array}{lll} C_{e}H_{s}(CH_{s})_{4} & C_{e}H_{s} \left\{ \begin{smallmatrix} C_{s}H_{6} \\ (CH_{s})_{2} \end{smallmatrix} \right. & C_{e}H_{4} \left\{ \begin{smallmatrix} C_{2}H_{5} \\ C_{2}H_{5} \end{smallmatrix} \right. & C_{e}H_{4} \left\{ \begin{smallmatrix} C_{2}H_{7} \\ CH_{3} \end{smallmatrix} \right. & C_{e}H_{5} \cdot C_{4}H_{9} \\ 3 \text{ Isomerides} & 6 \text{ Isomerides} \end{array}$$

(a) Tetramethyl Benzenes, $C_aH_a(CH_a)_4$. The three bodies possible theoretically are known. Symmetrical Durene [1,2,4,5], present in coal tar (A. 18, 3034), is formed from 6-brom-pseudocumene and 4,6-dibrom-m-xylene, by means of CH_aI and sodium; and from toluene by CH_aCl and $AlCl_a$, as well as from penta- and hexamethyl benzene, by means of Al_aCl_a . Nitric acid oxidizes it to durylic and cumidic acids, $C_aH_a(CH_a)_a$. ($CO_aH)_a$ (the symmetrical constitution of durene is concluded from this) (B. 11, 31). Durene is converted by concentrated sulphuric acid into hexamethyl benzene and the sulphonic acids of prehaited pseudocumene and isoxywlene which can be zene, and the sulphonic acids of preinitol, pseudocumene, and isoxylene, which can be separated by means of their amides. Penta-methyl and penta-ethyl benzene undergo similar transpositions.

Isodurene, [1,2,3,5]- or unsymmetrical tetramethyl benzene, is obtained from brommesitylene with CH₂I and Na (its constitution follows from this (B. 27, 3441)); also from camphor by the action of ZnCl₂ or iodine (B. 16, 2259). The oxidation of

isodurene with nitric acid yields 3-isodurylic acid, CaH2(CH2)2. CO2H (B. 15, 1853), and at last mellophanic acid.

Prehnitol, [1,2,3,4] or v-Tetramethyl Benzene, is produced by the action of methyl iodide and metallic sodium upon 2-brom-pseudocumene and 2,4-dibrom-metaxylene (B. 21, 2821). Its oxidation by nitric acid produces prehnitylic acid, CaH, (CH,) . O.H

(B. 19, 1214) and prehnitic acid, C₈H₁(CO₂H)₄.

(b) 4-Dimethyl Ethyl Benzenes: [1,2,4], boiling at 189°, and [1,3,4] at 184°, and [1,4,3] at 185°, are obtained by the action of ZnCl₂ or iodine upon camphor (B. 23, 988, 2349). The [1,3,5]-body, boiling at 185°, is produced when H₂SO₄ acts upon acetone and methylethyl ketone (B. 18, 666; 25, 1533).

(c) The three diethyl benzenes yield, first, ethyl benzoic acids and then phthalic

acids when they are oxidized.

(d) Methyl·n-propyl Benzenes: The ortho-body boils at 181°, the meta- at 177°, and the para- at 183°. They result from the action of C₂H₇I and Na upon o-, m-, and p-bromtoluene (B. 24, 443, 1649; 29, R. 417).

(e) Methyl-isopropyl Benzenes: Only the m- and p-bodies are known. The latter is the important cymene. m-Methyl-isopropyl

benzene occurs in the light resin oil (A. 210, 10).

Cymene = [1,4]-Methyl-isopropyl Bensene (see table, p. 53) occurs in Roman caraway oil (from Cuminum cyminum), together with cumic aldehyde, and in the oil from the seeds of Cicuta virosa, in the oil of Ptychotis ajowan, in thyme oil, and in the oil from Eucalyptus globulus. It is produced on heating thymol, carvacrol, C₄H₃(OH). (CH₃). C₄H₇, and camphor, with P₂S₅, or with P₂O₅ (A. 172, 307); also from turpentine oil and other terpenes, C₁₀H₁₆, by the withdrawal of two hydrogen This is effected by heating with SO₄H₂, or with iodine. The production of cymene on boiling cumic alcohol, C₆H₄(C₃H₇). CH₂. OH (having the isopropyl group), with zinc dust is especially interesting, as is its formation from geranial (p. 42). Cymene may be synthetically prepared from p-brom isopropyl benzene by means of methyl iodide and This last reaction explains its constitution (Widman, B. 24, sodium. 439, 970, 1362).

Cymene is a pleasantly smelling liquid. The barium cymene sulphonate, $(C_{10}H_{13}SO_3)_2Ba + _3H_2O$, crystallizing in shining leaflets is characteristic.

Dilute nitric acid or the chromic acid mixture oxidizes cymene to paratoluic acid, CaH4(CH3). CO4H, and terephthalic acid; whereas in the animal organism or upon shaking with caustic soda and air, it is converted into cumic acid, $C_8H_4(C_3H_7)$. CO_3H .

When concentrated nitric acid acts upon cymene, the product is not nitrocymene, but

p-tolylmethyl ketone (B. 19, 558; 20, R. 373).

(f) Butyl Benzenes: n-Butyl benzene boils at 180°; isobutyl benzene at 167°; secondary butyl benzene, at 171°.

Tertiary Butyl Benzene boils at 167°. Bromine does not attack it in the cold or when exposed to sunlight (B. 23, 2412; 27, 1610).

Higher toluene homologues:

Hydrocarbons, C₁₁H₁₆: Pentamethyl Benzene (see table, p. 53) is produced together with hexamethyl benzene when AlCl₂ and methyl chloride act upon benzene, toluene, xylene, mesitylene, etc. (B. 20, 896). For its deportment toward concentrated

sulphuric acid see durene (p. 55).

[1,3,5]-Diethylmethyl Benzene, boiling at 200°, results from the action of sulphuric acid upon acetone and methylethyl ketone. [1,2,4,5] Trimethylethyl Benzene, Ethyl Pseudocumene, boils at 207° (B. 25, 1530). Ethyl Mesitylene boils at 208° (B. 29, 2459). [1,3]-Methyl-tert.-butyl Benzene, boiling at 185-187°, occurs in the essence of resin, the distillation product obtained from pine resin, and is

obtained from the interaction of toluene, isobutyl bromide, and Al₂Cl₂. Its trinitroderivative is the artificial musk (B. 27, 1606).

Hydrocarbons, C₁₁H₁₈.—Hexamethyl Benzene (see table, p. 53) is formed by the polymerization of crotonylene on shaking with sulphuric acid, and by heating xylidene hydrochloride and methyl alcohol to 300°. For additional methods of formation see durene and pentamethyl benzene. It does not dissolve in sulphuric acid, as it is incapable of forming a sulpho-acid. Potassium permanganate oxidizes it to benzene hexacarboxylic acid, C₆(CO₂H)₆ (mellitic acid).

p-Di-n-propyl Benzene, from p-dibrom-benzene, boils at 219°. p-n-Propyl-iso-propyl Benzene, from cumyl chloride and zinc ethyl, boils at 212°. Nitric acid oxid-

izes both to n-propyl benzoic acid, which is isomeric with cumic acid.

Propyl Mesitylene boils at 221° (B. 29, 2459). [1,3,5]-Triethyl Benzene, from ethyl methyl ketone by the action of sulphuric acid, boils at 218°. [1,2,3,4]-Tetraethyl Benzene boils at 251°. [1,2,4,5] Tetraethyl Benzene melts at +13° and boils at 250°. Pentaethyl Benzene (see table, p. 53). Hexaethyl Benzene (see table, p. 53) is obtained from C₆H₆, C₃H₅Br, and Al₂Cl₆ (B. 16, 1745; 21, 2819). The following mono- and dialkylic benzenes with long chains have been prepared by

Fittig's reaction from brombenzene and bromtoluene:

n-Octyl Benzene, boiling at 262°; Cetyl Benzene, C₆H₅. C₁₆H₃₃, melting at 27° and boiling at 230° (15 mm); o-Methyl Cetyl Benzene, melting at 8-9° and boiling at 239° (15 mm.); m-Methyl Cetyl Benzene, melting at 10-12° and boiling at 237° (15 mm.); p-Methyl Cetyl Benzene, melting at 27° and boiling at 240° (15 mm.); Octadecyl Benzene, melting at 36° and boiling at 249° (15 mm.) (B. 21, 3182).

2. HALOGEN DERIVATIVES OF THE BENZENE HYDRO-CARBONS.

A. BENZENE HALOGEN SUBSTITUTION PRODUCTS.

Benzene being a cyclic triolefine, it can take up six atoms of chlorine or bromine in the sunlight. The products are benzene hexachloride and benzene hexabromide. These bodies will be discussed later as cyclohexane derivatives, following hexahydro-benzene. The hydrogen atoms in the benzene nucleus, however, are very easily replaced by chlorine and bromine—in fact, more readily than the hydrogen of the paraffins.

Properties and Deportment.—The benzene halogen derivatives are in part colorless liquids, and partly colorless, crystalline bodies. They have a faint, but not disagreeable odor. They are insoluble in water, but dissolve readily in other solvents, and volatilize without decomposition. para-bodies of the benzene dihaloids are solids at the ordinary temperature. Their melting points lie higher than those of the ortho- and

meta-compounds, while their boiling points are lower.

The intimate union of the halogen atoms to the benzene nucleus is They are not displaced, or, at least, with great difficulty, by caustic potash (B. 18, 335; 20, R. 712), by ammonia, cyanide of potassium, etc. (Compare the alkylogens, 1, 139.) Metallic sodium withdraws the halogens particularly from brom- and iodbenzenes. This behavior is especially important in the synthesis of the benzene hydrocarbons (p. 50). The reactivity of chlor-, brom-, and iodbenzene with piperidine, resulting in the formation of *phenyl piperidine* is peculiar (B. 21, 2279; compare also the nitrohalogen benzene derivatives, p. 67). Sodium amalgam in alcoholic solution or hydriodic acid and phosphorus reduce the halogen substitution products to benzene.

Fluorbenzenes result when hydrofluoric acid is poured upon benzene diazopiperidides (Wallach, A. 235, 258; 243, 221):

$$C_6H_5N = N - NC_5H_{10} + 2HFI = C_6H_5FI + N_2 + NH \cdot C_5H_{10} \cdot HFI$$
.

Fluorbenzene, C₆H₅Fl, boiling at 85°, specific gravity 1.0236 (20°/4°), was obtained by heating fluorbenzoic acid with hydrochloric acid. p-Difluorbenzene, C₆H₄[1,4]Fl₂, boils at 88° and has the specific gravity 1.11.

Chlorbenzenes.—Methods of Formation.—1. Free chlorine acts sluggishly upon benzene. The action is accelerated by iodine, molybdenum chloride, MoCl₅, and ferric chloride, which is particularly well suited for this purpose.

2. The hydroxyl groups of the free phenols are replaced with difficulty by chlorine when phosphorus pentachloride is the reagent. This substitution occurs more readily in the case of the nitrophenols.

3. A very important method that is particularly adapted for the preparation of chlorbenzenes and aromatic halogen derivatives consists in the transformation of the diazo-compounds. The latter are obtained from the amido-bodies, which are the nitro-reduction products. Atomic rearrangement does not occur in these reactions. In the decomposition of the diazo-body the chlorine enters the position which the diazo-, the amido-, and the nitro-group previously held:

$$C_6H_5N_2Cl = C_6H_5Cl + N_2$$

Diazobenzene
Chloride.

Knowing, therefore, when working with the di- and poly-substitution products, the constitution of one of the bodies thus changing, that of the other is necessarily established.

Name.	FORMULA.	М. Р.	B. P.	DENSITY.
Monochlorbenzene, [1,2]-(o)-Dichlorbenzene, [1,3]-(m) Dichlorbenzene, [1,4]-(p)-Dichlorbenzene, [1,2,3]-(v)-Trichlorbenzene, [1,2,4]-unsym. Trichlorbenzene, [1,3,5]-sym. Trichlorbenzene, [1,2,3,4]-v-Tetrachlorbenzene, [1,2,4,5]-sym. Tetrachlorbenzene,	C ₆ H ₄ Cl ₂ C ₆ H ₅ Cl ₃ C ₆ H ₂ Cl ₄ C ₆ H ₂ Cl ₄	45° + 53° 16° 63° 54° 46° 50° 137° 86° 226°	132° 179° 172° 172° 218° 213° 208° 254° 246° 2246° 326°	1.128 (o°)

The predominating product in the chlorination of chlorbenzene is p-dichlorbenzene. Very little o-dichlorbenzene results (B. 29, R. 648). p-Dichlorbenzene also results from the action of phosphorus pentachloride upon p-quinone (see this). The behavior of the dichlorbenzenes, when nitrated, is characteristic:

```
o-Dichlorbenzene yields [1,2]-dichlor-4-nitrobenzene, m. p. 43° m-Dichlorbenzene " [1,3]-dichlor-4- " m. p. 32° p-Dichlorbenzene " [1,4]-dichlor-3- " m. p. 55°
```

Hexachlorbenzene, Julin's chloride of carbon, has been prepared by the exhaustive chlorination of many alkyl benzenes and other derivatives of benzene (B. 29, 875). It is also produced when CHCl₂ and C₂Cl₄ are conducted through a tube heated to redness.

Brombenzenes are prepared just like the chlorine substitution products:

(1) By direct substitution by means of bromine carriers, such as aluminium bromide (B. 10, 971); (2) from phenols; (3) from diazo-derivatives (p. 58):

NAME.	FORMULA.	М. Р.	В. Р.	DENSITY.
Monobrombenzene,	C.H.Br	-31°	155°	1.517 (0°)
[1,2]-o-Dibrombenzer.e,	C _a H _a Br _e	ı°	2240	2.003 (0°)
[1,3]-m-Dibrombenzene,	. ". "	+ 1°	219°	"
[1,4] p-Dibrombenzene,		89°	219°	
[1,2,3] v-Tribrombenzene,		87°		
[1,2,4]-unsym. Tribrombenzene,		44°	275° 278°	1
[1,3,5]-sym. Tribrombenzene,		119°	278°	1
[1,2,3,4] v-Tetrabrombenzene,	C ₆ H ₂ Br ₄	98°		i
[1,2,3,5] unsym. Tetrabrombenzene,		98°	329°	
[1,2,4,5] sym. Tetrabrombenzene,		175°	_	[B. 28,191]
Pentabrombenzene,	C ₆ HBr ₅	260°	_	
Hexabrombenzene,	C ₆ Br ₆	ab. 315°		

In the bromination of hot benzene the chief product is the p-dibrom body, and very little of the o-derivative (B. 10, 1345). The nitration of these dibrombenzenes is characteristic for them:

```
o-Dibrombenzene yields [1,2]-dibrom-4-nitrobenzene, m. p. 58°.
m-Dibrombenzene yields (1) [1,3]-dibrom-4-nitrobenzene, m. p. 61°[chief product].
(2) [1,3]-dibrom-2-nitrobenzene, m. p. 82°[secondary product].
p-Dibrombenzene yields [1,4]-dibrom-2-nitrobenzene, m. p. 85°.
```

W. Körner utilizes the production of the tribrombenzenes from the three dibrombenzenes in deducing their constitution (p. 38). *Hexabrombenzene* is also formed upon heating CBr₄ to 300°.

Kekulé heated (200°) benzene with iodine and iodic acid, and thus obtained the iodbenzenes. The reaction proceeded in the sense of the equation (A. 137, 161):

$$5C_0H_0 + 4I + HIO_3 = 5C_0H_0I + 3H_2O.$$

They have been obtained more frequently from the corresponding amido-bodies by aid of the diazo-derivatives (p. 58):

Name.									FORMULA.	М. Р.	В. Р.		
Iodbenzene, [1,2] · (o) · Ibi-iodbenzene, [1,3] · (m) · Di-iodbenzene, [1,4] · (p) · Di-iodbenzene,	•	:	:	•	•	:	•	:	:	•	C _a H _a I _a	— 30° + 27° 40° 129°	188° 286° 285° 285°

Hexa-iodbenzene, C₆I₆, is formed in the exhaustive iodation of benzene carboxylic acids (benzoic acid, terephthalic acid) with iodine and fuming sulphuric acid. It consists of reddish-brown needles, which melt with decomposition from 140–150° (B. 29, 1631). See B. 29, 1405, for bromiodbenzenes.

Iodoso-benzene. Iodobenzene. Diphenyliodonium Hydroxide.—These remarkable bodies were obtained from *phenyliod-chloride* (Willgerodt, 1886), which contains two atoms of chlorine combined with iodine; it may be derived from iodine trichloride, ICl₃ (see Inorganic Chemistry).

Phenyliod-chloride, $C_6H_6ICl_2$, consists of yellow needles. It is produced when chlorine is conducted into a solution of iodbenzene in chloroform. When it is shaken with caustic alkali iodoso-benzene results:

$$C_6H_5ICl_2 + 2KI = C_6H_5IO + 2KI + H_2O.$$

Iodosobenzene, C₈II₈IO, is an amorphous substance. It explodes at about 210°. When it is treated with an acidulated solution of potassium iodide it gives off its oxygen with the separation of an equivalent amount of iodine:

$$C_6 II_5 IO + 2KI + 2CII_3 \cdot COOH = C_6 II_5 I + 2CH_3 COOK + 2I + H_2O.$$

It has a basic character and forms salts, which are derived from the hypothetical hydrate $C_6II_5I(OII)_2$ —c.~g., $C_6II_5I(OOC.CH_8)_2$; hence $C_6H_5ICl_9$ should be regarded as iodosobenzene hydrochloride.

Iodobenzene, C₆H₅IO₂, is formed when iodosobenzene is heated alone or boiled with water:

$$2C_6H_5IO = C_6H_5I + C_6H_5IO_2$$

or by the oxidation of iodosobenzene with hypochlorous acid, or upon treating phenyliod-chloride with a bleaching lime solution (B. 29, 1567). Iodobenzene explodes at 227-230°. Its deportment is like that of a superoxide.

Diphenyliodonium Hydroxide, (C₆H₅)₂IOH, is only known in aqueous solution. It is formed on shaking a mixture of iodoso and iodobenzene with moist silver oxide:

$$C_6H_5IO + C_6H_5IO_2 + AgOH = (C_6H_5)_2I \cdot OH + IO_3Ag.$$

Its iodide results on boiling iodobenzene with a solution of potassium iodide (B. 29, 2008). Diphenyliodonium hydroxide has a strong alkaline reaction and forms salts: $(C_6H_5)_2I.I.((C_6H_5)_2ICI.(C_6H_5)_2INO_9$, which recall the salts of thallium (compare ammonium compounds, I, p. 168; metallo-organic derivatives, I, p. 182). The carbonate and nitrate are very soluble; the chloride and bromide form white precipitates. Diphenyliodonium Iodide, $(C_6H_5)_2I.I.$, is polymeric with iodbenzene. It consists of yellow needles, which dissolve with difficulty in alcohol, and melt, with production of iodbenzene, at 175–176° (V. Meyer, B. 27, 1592; 28, R. 80).

B. HALOGEN DERIVATIVES OF THE ALKYL BENZENES.

Under the conditions observed with benzene itself—in the cold, in the presence of iodine, with molybdenum pentachloride, or ferric chloride—the atoms of chlorine or bromine enter the nucleus of the alkyl benzenes. The aromatic substitution products result. Thus, toluene affords:

In the case of boiling benzene homologues the substitution takes place almost exclusively in the hydrogen of the side-chain, and *aliphatic* substitution products result. Thus, toluene yields

These are compounds corresponding to:

and will be considered at the conclusion of the oxygen derivatives which correspond to them:

$$C_6H_5$$
. $CH_3OH \longrightarrow C_6H_5CHO \longrightarrow C_6H_5CO_3H$
Benzyl Alcohol Benzaldehyde Benzoic Acid.

into which they can be easily transformed, and from which they can be obtained by the use of phosphorus pentachloride.

In sunlight chlorine and bromine also act substitutingly in the cold upon the aliphatic side-chains (B. 20, R. 530). Chlorine converts boiling isopropyl benzene into p-chlorisopropyl benzene (B. 26, R. 771). Phosphorus trichloride also attacks the alkyls of the alkyl benzenes at the boiling temperature.

The other two methods which may be considered in the production of halogen derivatives of benzene—the action of phosphorus halides upon oxybenzenes and the transformation of corresponding diazo-bodies—yield alkyl benzenes, with substitutions in the nucleus. Naturally, a substitution can occur both in the nucleus and in the aliphatic residue of the same alkyl benzene. The halogen atoms which have entered the side-chain are always reactive, and can readily be exchanged for radicals, whereas the halogen atoms which have entered the benzene nucleus are very intimately combined. The aromatic mono-halogen derivatives of the alkyl benzenes, especially the bromalkyl benzenes, have been largely used in the synthesis of higher alkyl benzenes, following the method discovered by Fittig (p. 50). The oxidation of the side-chains to carboxyl groups is very important for the determination of constitution. It is in this way that any halogen atoms present in the side-chains can be determined (p. 52).

Sodium amalgam in alcoholic solution will replace the halogen atoms with hydrogen. Hydriodic acid will do the same.

The aromatic halogen substitution products of the alkyl benzenes are exceedingly numerous. Their simplest representatives are the monohalogen toluenes, which are tabulated for more complete review:

NAME.			FORMULA.	М. Р.	B. P.			
1,4], p-Fluortoluene, 1,2], o-Chlortoluene, 1,3], m-Chlortoluene, 1,4], p-Chlortoluene, 1,2], o-Bromtoluene, 1,4], p-Bromtoluene, 1,4], p-Bromtoluene, 1,2], o-Iodtoluene, 1,4], p-Iodtoluene, 1,4], p-Iodtoluene,						CH ₃ [1] C ₄ H ₄ [4] F1 CH ₃ [1] C ₄ H ₄ [2] Cl CH ₃ [1] C ₄ H ₄ [3] Cl CH ₃ [1] C ₄ H ₄ [2] Br CH ₄ [1] C ₄ H ₄ [2] Br CH ₅ [1] C ₄ H ₄ [3] Br CH ₅ [1] C ₄ H ₄ [2] I CH ₃ [1] C ₄ H ₄ [2] I CH ₃ [1] C ₄ H ₄ [3] I CH ₅ [1] C ₄ H ₄ [3] I CH ₅ [1] C ₄ H ₄ [3] I CH ₅ [1] C ₄ H ₄ [4] I	-34° -48° + 7° -26° -40° +28° -35°	117° 156° 150° 163° 181° 183° 184° 204° 211°

p-Fluortoluene has been prepared by the method used for fluorbenzene. The chlorination and bromination of toluene in the cold, or in the presence of iodine or Fe₂Cl₄, results in the formation of para- and ortho-derivatives in almost equal quantities. p-Chlortoluene can be separated from its ortho-isomeride by heating with sulphuric acid to 150°, when the o-body passes into its sulpho-derivative.

All the monochlor-, monobrom-, and monoiod-toluenes are obtained pure by decomposing the diazo-compounds made from the three amido-toluenes or toluidines (p. 58). o- and p-Toluidines are easily obtainable from the corresponding nitrotoluenes (p. 68). m-Bromtoluene has been prepared by brominating acet-p-toluidine to m-brom-acet-p-

toluidine, and then replacing the amido-group by hydrogen (p. 51).

m. Chlortoluene has also been prepared from 3-methyl-Δ₂-keto-R-hexene (1, p. 325), into which methylene diacetoacetic ester can be easily converted.

This is accomplished by first preparing, with the aid of phosphorus pentachloride, tetrahydro-m-dichlortoluene, which decomposes into hydrogen chloride and dihydro-m-chlortoluene. Bromine with draws two hydrogen atoms from this body and m-chlortoluene results (B. 27, 3019):

If we start with ethidene diacetoacetic ester, the product will be [1,3,5]-chlor-mxylene (B. 29, 310). [1,3,6]-Chlorcymene has been similarly prepared from menthone or ketohexahydrocymene (B. 29, 314).

The iodoso- and iodo-compounds corresponding to p-iodtoluene are known (B. 26,

35**8; 27,** 1903).

The conversion of the halogen toluenes into solid nitrohalogen toluenes and their oxidation to halogen benzoic acids of known constitution are distinguishing characteristics. When heated with a chromic acid mixture (see aromatic acids) the p- and m-derivatives are oxidized to the corresponding substituted benzoic acids, whereas the o-derivatives are attacked with difficulty and completely destroyed. When boiled with dilute nitric acid, with potassium permanganate, or ferricyanide of potassium, all three isomerides (even the ortho) are oxidized to acids.

Six isomeric aromatic dihaloid toluenes, with similar halogen atoms, are possible. The six dichlortoluenes are known (B. 29, R. 867). They are isomeric with benzal chloride, C₄H₅CHCl₂, and with the chlorbenzyl chlorides, ClC₆H₄CH₂Cl. All of the six isomeric dibromtoluenes have also been prepared. Pentabromtoluene has been obtained from

suberane and bromine (p. 28).

The appended table contains the easily accessible bromine derivatives of the polymethyl benzenes:

It is also remarkable that concentrated sulphuric acid is even capable of carrying bromine atoms as it does alkyl groups (p. 51). Thus, concentrated sulphuric acid first converts monobromdurene into dibromdurene, and then into durene (B. 25, 1526).

3. NITROGEN DERIVATIVES OF THE BENZENE HYDRO-CARBONS,

In which the nitrogen-containing residue is joined to the benzene nucleus by means of or through nitrogen.

These compounds can be classified according to the number of nitrogen atoms contained in the residues. The first class embraces only those in which a single nitrogen atom is present. The *nitro*-compounds are placed at the head of this division. They are very important benzene derivatives. They constitute the starting-bodies for the preparation of the succeeding groups. The *amido*-compounds attach themselves to them. In this class belong the generators of numerous coal-tar dyes and aromatic derivatives having therapeutic value. The *nitroso*- and β -hydroxylamine bodies constitute the transition between these two groups.

In the second class are those compounds whose nitrogen residues contain two and more nitrogen atoms in union with each other. The nitro-amines, the nitroso-β-hydroxylamines, the nitrosamines, the azoxy-derivatives, the hydrazines, the diazo- and the azo-compounds contain two nitrogen atoms. The nitrosohydrazines, the diazoamido-bodies, and the azo-imido compounds contain three nitrogen atoms, while four nitrogen atoms

are present in the diazohydrazido- or buzylene derivatives, and the tetrazones, and five in the disazoamido-compounds.

The study of some of these classes has also been of the greatest importance for the chemistry of inorganic nitrogen compounds. If we imagine these eighteen groups of aromatic nitrogen bodies derived from inorganic nitrogen-containing substances, whose formulas can be obtained by the substitution of hydrogen for the aromatic residues, it will be discovered that six of these eighteen forms occur free or in the form of inorganic derivatives of known bodies. In the following table they appear in black-face type:

I.	Nitro-compounds,		derived	from	H.NO,
	Nitroso-compounds,		4.6	**	H. NO
	β-Hydroxylamine compounds,		66	"	H.NHOH
4.	Amido-compounds,		"	"	H.NH.
5.	Nitroamines,		66	6.6	H.NH.NO.
6.	Nitroso-\(\beta\)-hydroxylamines,		"	46	H. N(OH). NO
	Nitrosamines,		"	"	H.NH.ŃO
	Azoxy-compounds,		"	"	$H. N \stackrel{\frown}{\searrow} N. H$
0.	Hydrazines,	•	"		H.NH.NH.
10.	Diazo-compounds,	•	"	"	H.N=N.OH
	Azo-compounds,		"	44	H.N=N.H
	Nitrosohydrazines,		"	"	H.N(NO).NH
12.	Diazoamido-compounds,	•	"	44	H.N=N.NH
14.	Diazo-oxyamido-compounds,		"	"	HN = N - NHOH
	Azoimido-compounds,		**	"	$H.N < N \\ N$
16.	Diazohydrazo- or Buzylene compounds,		46	"	H.N = N.NH.NII
	Tetrazones,		"		H.NH.N = N.NH.H
	Disdiazoamido derivatives,		"	"	H.N=N.NH.N=N.H.

The first three groups will be treated in the preceding order. The nitroso- β -hydroxylamines (6) attach themselves to the β -hydroxylamines (3). Then follow the amido-derivatives (4), the nitrosamines (7), the nitrosamines (5), the diazo-derivatives (10), the diazoamido-bodies (13), the disdiazoamido- (18), the diazo-oxyamido- (14), and the azoimido-compounds (11). The next in order are the azoxy- (8) and the azobodies (11). The last to be considered are the hydrazines (9), the nitrosohydrazines (12), the tetrazones (17), and the diazohydrazo- or buzylene derivatives (16). This arrangement is justified by the genetic relations of the individual classes of bodies to one another, and they should have preference over the purely systematic arrangement.

1. NITRO-DERIVATIVES OF BENZENE AND THE ALKYL BENZENES.

Benzene and alkyl benzenes containing hydrogen in the nucleus readily yield nitro-derivatives by the action of nitric acid:

$$C_6H_6 + NO_2OII = C_6H_6NO_2 + H_2O_2$$

These compounds are more or less yellow in color; the nitrogen of

the nitro-group is in direct union with a carbon atom, as in nitromethane. By reduction they yield amido-bodies:

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O.$$

In a preceding section mention was made that all of the hydrogen in benzene could be replaced by chlorine or bromine. The case is different on introducing nitro-groups. The first two nitro-groups can be introduced quite easily, the third with difficulty, and thus far not more than three nitro-groups have been introduced into one benzene residue.

A mixture of nitric acid (1 part) and sulphuric acid (2 parts) acts more energetically than nitric acid alone, as the second acid combines with any water that may be formed in the reaction. Di- and tri-nitro-compounds are the chief products. The nitration is considerably moderated by previously dissolving the substance in glacial acetic acid. The more alkyl groups there are in a benzene hydrocarbon, the more readily will it be nitrated.

The production of nitrophenols in the nitration of benzene hydrocarbons may be explained by assuming an addition of nitric acid at the double union of the benzene ring, with the splitting-off of nitrous acid on the one side and water on the other (B. 24, R. 721). On heating alkyl benzenes with dilute nitric acid, the nitro-group enters the aliphatic side-chain. The resulting bodies will be more fully described after the corresponding alcohols (B. 27, R. 193). The aromatic amines, obtained by the reduction of nitro-compounds, can easily be changed to the latter through the diazo-derivatives, when nitrous acid salts yield nitro-bodies with cuprous oxide. Nitro-compounds have also been obtained by the direct oxidation of amines—e. g., nitrobenzene, by the action of potassium permanganate upon aniline.

Properties and Deportment.—The nitrohydrocarbons are only slightly soluble in water, but they do dissolve in concentrated nitric acid, and are precipitated from this solution by water. They are very soluble in alcohol, ether, glacial acetic acid, etc. The melting points of the nitrobodies are usually higher than those of the corresponding bromine derivatives. Their easy reduction is especially interesting.

The β-phenylhydroxylamines have been found to be intermediate products in their conversion into amido-derivatives. Just as two kelone molecules in their reduction combine to a pinacone molecule, so two nitrobenzene molecules, by reduction with alcoholic potash, give off oxygen and form azoxybenzene, which can easily be reduced to azo- and hydrazobenzene.

These relations are made evident in the following diagram:

$$C_{e}H_{5}NO_{2} \begin{cases} \begin{array}{c|cccc} & C_{e}H_{5}NHOH & C_{e}H_{5}NH_{2} & C_{6}H_{4} & \begin{bmatrix} 1 \end{bmatrix}OH \\ APPhenylhydroxylamine & Anilline & P-Amidophenol \\ \hline & C_{e}H_{5}N & C_{e}H_{5}N & C_{6}H_{5} & NH \\ \hline & C_{e}H_{5}N & C_{e}H_{5}N & C_{6}H_{5} & NH \\ \hline & C_{e}H_{5}N & C_{e}H_{5}N & H \\ \hline & Azoxybenzene & Azobenzene & Hydrazobenzene. \\ \end{array}$$

In the electrolytic reduction of nitro-bodies dissolved in sulphuric acid amidophenols are formed together with the amidohydrocarbons. This is due to a rearrangement of the unstable β -phenylhydroxylamines, or rearrangement and decomposition of intermediate azoxy-derivatives (B.

29, R. 230). In hydrochloric acid solution it is very probable that p-chloranilines are similarly produced (B. 29, 1894).

Because of the ready reduction of the nitro-bodies to compounds, many of which meet with the most varied application in the coal tar color manufacture, there attaches to them the importance of the more valuable and indispensable intermediate products.

When the polynitrohydrocarbons are oxidized with an alkaline ferricyanide solution they are changed to polynitrophenols. The nitro-groups in many polynitrohydrocarbons are exchanged for chlorine when they are heated to 200–300° with hydrochloric acid. Sometimes further chlorination occurs to a certain degree (B. 29, R. 594).

Nitrobenzenes.—The following table contains the melting and boiling points of the six known nitrobenzenes:

Name.	FORMULA.	М. Р.	В. Р.
Nitrobenzene, [1,2]-, o-Dinitrobenzene, [1,3]-, m-Dinitrobenzene, [1,4]-, p-Dinitrobenzene, [1,2,4]-, unsym. Trinitrobenzene, [1,3,5]-, sym. Trinitrobenzene,	C.H.(NO.).	+ 3° 116° 90° 172° 57° 121°	205° 319° (773 mm.) 303° (771 mm.) 299° (777 mm.)

Nitrobenzene, C₆H₅NO₂, was discovered in 1834 by Mitscherlich (Pogg. Ann. 31, 625) on treating benzene with nitric acid. It is also produced in the oxidation of aniline (p. 74). It is technically prepared on a large scale, and worked up into aniline and azobenzene. In making it commercially a mixture of nitric and sulphuric acids is allowed to run with constant stirring into benzene. The benzene is contained in castiron cylinders (G. Schultz, Chemie des Steinkohlentheers).

Nitrobenzene is a faintly yellow-colored, strongly refracting liquid, possessing an odor resembling that of benzaldehyde or oil of bitter almonds. Its dilute aqueous solution has a sweet taste (B. 27, 1817) and a specific gravity of 1.20 at 20°. It is poisonous in its action, particularly when its vapor is inhaled. Nitrobenzene is used not only in the preparation of colors, but also in perfumery, and to impart to soap the odor of bitter-almond oil (essence of mirbane). It is quite frequently employed in the laboratory as a solvent. Its behavior when reduced has already been referred to (p. 65); its most valuable technical product is aniline (p. 74). In many important reactions nitrobenzene serves as an oxidant (see rosaniline and quinoline).

Dinitrobenzenes, C₆H₄(NO₂)₂.—The melting and boiling points are given above. The three dinitrobenzenes are produced if in the nitration with fuming nitric acid the mixture be boiled a short time. On crystallizing from alcohol, the m-compound, formed in greatest quantity, separates first, whereas the o- and p-dinitro-derivatives remain in solution (B. 7, 1372). The meta-body is used in the color industry for the preparation of m-phenylenediamine.

p-Dinitrobenzene can also be obtained by oxidizing p-quinone dioxime (see this); the o-dinitrobenzene from the residues in the preparation of m-dinitrobenzene by solution in twice their weight of boiling nitric acid and pouring this into five to six times its volume of cold nitric acid, when the o-dinitrobenzene will separate in crystals (B. 26, 266).

By half reduction the dinitrobenzenes yield nitroanilines, which connect genetically the phenylenediamines with the dibrombenzenes and the benzene dicarboxylic acids, or phthalic acids (p. 38).

Ortho-dinitrobenzene crystallizes in plates, yields o-nitrophenol when boiled with caustic soda, and o-nitraniline when heated with alcoholic ammonia. Other aromatic o-dinitro-bodies behave similarly.

Metadinitrobenzene, when heated with potassium ferricyanide and caustic soda, forms a- or [1,OH,2,4]-dinitrophenol and β - or [1,OH,2,6]-dinitrophenol. m-Dinitrobenzene, heated with alcoholic potash, has one of its nitro-groups replaced by ethoxyl, with the simultaneous entrance of a cyanogen group and the production of [2]-nitro-[6]-ethoxybenzonitrile (B. 17, R. 19). It unites with alkali bisulphite, with simultaneous reduction and sulphonation, to form m-nitraniline-p-sulphonic acid (B. 29, 2448).

Paradinitrobenzene forms colorless needles. m- and p-Dinitrobenzenes form additive compounds with naphthalene (B. 16, 234). When the dinitrobenzenes are heated with chlorine or bromine to 200°, the nitro-groups are wholly or partially replaced by halo-

gens (B. 24, 3749).

Trinitrobenzenes.—Melting points, see above. [1,3,5]-, sym. Trinitrobenzene is obtained from m-dinitrobenzene, and synthetically on acidulating sodium nitromalonic aldehyde (B. 28, 2597). [1,2,4]-, unsym. Trinitrobenzene is produced by heating p-dinitrobenzene with nitric acid and pyrosulphuric acid to 180°. sym. Trinitrobenzene may be oxidized to picric acid, or [1,0H,2,4,6]-trinitrophenol. It forms additive compounds with aniline, naphthalene, etc. m- and p-Dinitrobenzene, trinitrotoluene, etc., yield similar combinations (B. 13, 2346; 16, 234). Aqueous alkalies impart orange-yellow colorations to sym. trinitrobenzene. These are probably due to the formation of unstable salts resulting from the replacement of benzene hydrogen by metals (B. 29, 848; R. 39).

Nitro-haloid Benzenes.

Formation: (1) Upon nitrating chlor-, brom-, and iod-benzene, p- and o-mononitro-products result; the first in larger quantity. (2) On heating the dinitrobenzenes with bromine or chlorine a nitro-group can be replaced by a halogen. (3) Or the dinitrobenzenes are changed to nitranilines and the amido-group replaced by halogens, effected by means of the diazo-compounds. (4) PCl₆ also converts nitrophenols into chlornitroderivatives. The nitro-haloid benzenes afford the transition from the dinitro-, nitroamido-, to the haloid-amido- and dihalogen benzenes. They are consequently especially important for the recognition of the connection of the various disubstitution products of benzene:

$$C_{\mathbf{6}}H_{\mathbf{4}} < \overset{\mathbf{NO_2}}{\overset{}{\mathbf{NO_2}}} \longrightarrow C_{\mathbf{6}}H_{\mathbf{4}} < \overset{\mathbf{NO_2}}{\overset{}{\mathbf{NH_2}}} \longrightarrow C_{\mathbf{6}}H_{\mathbf{4}} < \overset{\mathbf{NO_2}}{\overset{}{\mathbf{Br}}} \longrightarrow C_{\mathbf{6}}H_{\mathbf{4}} < \overset{\mathbf{NH_2}}{\overset{}{\mathbf{Br}}} \longrightarrow C_{\mathbf{6}}H_{\mathbf{4}} < \overset{\mathbf{Br}}{\overset{}{\mathbf{Br}}}.$$

The isomeric mononitro-chlor-, brom-, and iod-benzenes have the following melting points:

Meta-chlornitrobenzene occurs in two physical modifications; if rapidly cooled after fusion, it melts at 23.7°, but in a short time reverts to the stable modification, melting at 44.2°.

Of the numerous nitro-haloid benzenes which have been prepared, mention may yet be made of [1,Cl,3,4]-Dinitro-chlorbenzene, which has been obtained, in three very

similar modifications, melting at 36.3°, 37°, and 38° (B. 9, 760), and also of Trinitro-chlorbenzene, $C_2H_2Cl(NO_2)_3$ (1,3,5,4,Cl), Picryl Chloride, obtained from picric acid by the action of PCl_3 . It melts at 83°. It is converted into picramide, $C_4H_2(NH_2)$ (NO_3), with ammonia, and into picric acid when boiled with soda.

The halogen atom in every monohaloid nitrobenzene is always more easily exchanged the more numerous the nitro-groups are. Picryl chloride, in its deportment, approaches the acid chlorides. Trichlordinitrobenzene melts at 130° (B. 29, R. 1155).

Nitrotoluenes.—[1,2], o-Nitrotoluene, $CH_3[1]C_6H_4[2]NO_2$, melting at 10.5°, boiling at 218°, and [1,4]-,p-Nitrotoluene, CH,[1] C₆H₄[4]NO₂, melting at 54° and boiling at 230°, are produced in the nitration of toluene. They are separated by fractional distillation, and when reduced, yield the technically important toluidines. If the nitration be carried on at -55°, five and a half times as much p- as o-nitrotoluene (B. 26, R. 362) will be produced. At higher temperatures fuming nitric acid produces chiefly p nitrotoluene; whereas, nitricsulphuric acid at lower temperature yields about 66 per cent. of o-nitrotoluene.

Further nitration of o and p-nitrotoluene produces [2,4]-dinitrotoluene, melting at 70°; [2,5]-dinitrotoluene, melting at 48° (B. 21, 433; 22, 2679), and [2,4,6]-trinitrotoluene, melting at 82°.

The conversion of o-nitrotoluene by bromine at 170° into dibromanthranilic acid is very remarkable:

$$C_aH_4(NO_2)CH_3 + 2Br_2 + 2H_2O = C_aH_2Br_2(NH_2)CO_2H + 2HBr.$$

Metanitrotoluene (1,3) is formed if acetparatoluidine, C_6H_4 $\begin{cases} CH_8\\ NH \cdot C_2H_8O_3 \end{cases}$ trated, and the amido-group replaced by hydrogen (B. 22, 831). It melts at 16° and boils at 230°. Further nitration of m-nitrotoluene produces [3,4]-dinitrotoluene,

melting at 61°, and [3,5]-dinitrotoluene, melting at 92° (B. 27, 2209).

Nitro-products of other Alkyl Benzenes.—The ease with which aromatic nitroderivatives are produced adapts many of them for the detection and recognition of their parent hydrocarbons. Some of them are:

[4] Nitro-o-xylene, $NO_2[4]C_6H_2[1,2](CH_2)_2$, melting at 29° (B. 17, 160; 18, 2670).

[2,4]-Dinitro-m-xylene, melting at 82°. [2,6]-Dinitro-m-xylene, melting at 93°. [2,4,6]-Trinitro-m-xylene, melting at 182° (B. 17, 2424). [2]-Nitro-p-xylene, boiling at 239° (B. 18, 2680). [2,6]-Dinitro-p-xylene, melting at 123°, and [2,3]-dinitro-p-xylene, melting at 93°, form a double compound, melting at 99° (B. 15, 2304). [2,3,6]-Trinitro-p-xylene melts at 137° (B. 19, 145). sym. Trinitrochlorxylene melts at 218° (B 28, 2047).

Nitromesitylene, NO₂[2]C₆H₂[1,3.5](CH₂)₃, melts at 44°. Dinitromesitylene melts at 86°. Trinitromesitylene melts at 232° (compare B. 29, 2201).

[3,5,6]-Trinitropseudocumene, (NO₂)₃[3,5,6]C₆[1,2,4](CH₂)₃, melts at 185°. [4,5,6]-Trinitro-v-trimethyl Benzene, (NO₂)₃[4,5,6]C₆[1,2,3](CH₂)₃, melts at 209° (B. 19, 2517).

Nitroprehnitol, NO₂[5]C₆H[1.2,3,4](CH₃)₄, melts at 61° (B. 21, 905). Dinitroprehnitol melts at 178°. Dinitro-isodurene, (NO₂)₃[4,6]C₆(1,2,3.5)(CH₃)₄, melts at 156°. Dinitrodurene, (NO₂)₂[3,6]C₆[1,2,4,5](CH₃)₄, melts at 205°. [2,4,6]-Trinitro-ψ-butyl Toluene, (NO₂)₃[2,4,6]C₆H[1]CH₃[3]C(CH₃)₃, melting at 96-97°, smells intensely like musk, and occurs in commerce as artificial musk (B. 24,

2832).

REGULARITIES IN SUBSTITUTION.

Formation of Diderivatives.—In the chlorination and bromination of benzene and toluene, as well as in the nitration of monohaloid benzenes and toluene, the products are almost exclusively p- and o-diderivatives, whereas in the nitration of benzene m-dinitrobenzene is the predominating product. Phenol, aniline, etc., behave like toluene; the first products are p- and o-diderivatives. Benzene-sulphonic acid, C₆H₅CO₂H; benzole acid, C₆H₅CO₂H; benzaldehyde, C₆H₆CHO; benzonitrile, C₆H₅CN; acetophenone, C₆H₅. CO. CH₈, and some additional compounds with negative side-chains yield meta-derivatives chiefly. The substituents present in the mono-derivatives exert, therefore, a definite, directing influence upon the position in which further substitution is to occur. It is not, however, immaterial in what succession or order the substituents are introduced. When chlorbenzene is nitrated, the principal product is an introchlorbenzene, while in the chlorination of nitrobenzene it is chiefly m-nitrochlorbenzene which results.

See B. 23, 130, upon the dependence of the processes of substitution upon the atomic and radical magnitude of the substituents.

Rule of Crum Brown and J. Gibson.—If the hydrogen compound of the atom or radical, which in the mono-derivative has entered the benzene nucleus, cannot be directly (i. e., in one operation) oxidized to the corresponding hydroxyl derivative, then in further substitutions o- and p-derivatives result, while in the opposite case m-derivatives predominate (B. 25, R. 672).

Formation of Triderivatives.—By the further substitution (chlorination, nitration) of the ortho- and para-di-derivatives, the replacing groups enter the para- or ortho-position, so that di-derivatives (1,2) and (1,4) yield the same triderivatives (1,2,4) (A. 192, 219). The meta-di-derivatives [1,3] yield [1,3,4]- and [1,2,3]-tri-derivatives. When both substituting groups are of a strongly acid character, as in m-dinitrobenzene, then [1,3,5]-derivatives result.

Formation of Tetra-derivatives.—If an unsymmetrical tri-derivative (1, 2, 4) be further substituted, unsymmetrical tetra-derivatives (1, 2, 4, 6) are generally produced. Thus, from aniline, C_6H_5 . NH₂, phenol, C_6H_5 . OH, etc., we obtain compounds like C_6H_2 -Cl₃. NH₂ and C_6H_5 (NO₂)₃. OH (1, 2, 4, 6)—NH₂ or OH in 1, in which the entering groups occupy the meta-position (2, 4, 6 = 1, 3, 5) with reference to each other. By the elimination of the OH and NH₃ groups in them, we obtain symmetrical tri-derivatives, $C_6H_3X_3$ (1, 3, 5).

2. NITROSO-DERIVATIVES OF BENZENE AND THE ALKYL BENZENES.

Mononitroso-derivatives of the benzene hydrocarbons are universally prepared by oxidizing the corresponding β -hydroxylamine derivatives (see below) in the cold with potassium bichromate and sulphuric acid:

$$C_aH_bNHOH + O = C_aH_bNO + H_sO$$
.

They consist of colorless crystals, are very volatile, and in a fused or dissolved condition are green in color. They yield nitro-bodies upon oxidation, and amido-derivatives when they are reduced. They condense with aromatic amines with the exit of water, and yield azo-compounds, while with β -phenylhydroxylamines they form azoxy-bodies and with hydroxylamine the so-called isodiazobenzenes (Bamberger, B. 28, 245, 1218; 29, 102):

Nitrosobensene, C₈H₈NO, melting at 68°, was first obtained in solution by the action of nitrosyl bromide upon mercury diphenyl (v. Baeyer, 1874; see B. 30, 506). It is made by oxidizing β -phenylhydroxylamine, and is produced in small amounts, together with other products, in the oxidation of diazobenzene chloride, and by the action of alkalies upon diazobenzene perbromide, as well as in the distillation of azoxybenzene (B. 27, 1182, 1273). In addition to the preceding reactions mention may be made of the union of nitrosobenzene with phenylhydrazine, forming diazo-oxyamido-benzene, C₆H₅N: N. N(OH). C₆H₅ (B. 29, 103). Two molecules of nitric oxide and nitrosobenzene unite to form diazobenzene nitrate (B. 30, 512).

o., m., p.Nitrosotoluene, CH₃, C₈H₄NO, melt at 72°, 53°, 48°. p.Chlor- and p.Brom-nitrosobenzene melt at 87° and 92°.

p-Dinitroso-derivatives result upon oxidizing p-quinodioximes with potassium ferri-

cyanide in alkaline solution—e.g.
p-Dinitrosotoluene, CH₃[1]C₈H₂[2,5](NO)₂, melting at 133°, from toluquinonedioxime, CH₃C₈H₃(NOH)₂, consists of yellow needles, with an odor like that of quinone. Fuming nitric acid converts them into p-dinitrotoluene, and with hydroxylamine hydrochloride they form toluquinone dioxime (B. 21, 734, 3319).

3. β-ALPHYLHYDROXYLAMINES.*

These very reactive bodies have been obtained as intermediate products in the reduction of nitro- and nitroso-benzenes. They are very sensitive to alkalies, hence they are best prepared by aid of neutral reducing agents—for example, by the action of aluminium amalgam and water upon the ethereal solutions of the nitrobenzenes (B. 29, 494, 863, 2307). They reduce an ammoniacal silver solution, and also Fehling's solution.

β Phenylhydroxylamine, C₆H₆NHOH, melting at 81° (its chlorhydrate precipitated from ether is a white, crystalline mass), is rapidly oxidized in aqueous solution by the air to azoxybenzene, C_8H_5N O N. C_8H_5 , and by potassium bichromate and sulphuric

acid to nitrosobenzene. It combines to C₈H₈N CH.C₈H₅ (B. 29, 3037) with

benzaldehyde, with diazobenzene to diazo-oxyamido-benzene, and with nitrous acid to nitrosophenylhydroxylamine. Mineral acids rearrange β -phenylhydroxylamine into p-amidophenol; compare similar rearrangements of the aromatic nitramines (diazobenzene acid), nitrosoamines, chloramines, into p-nitro-, p-nitroso-, and p-chloranilines (see these).

 β o Tolylhydroxylamine is an oil. β m Tolylhydroxylamine melts at 68°. β p Tolylhydroxylamine, melting at 94°, is converted by dilute sulphuric acid into p-toluhydroquinone (B. 28, 245, 1218, R. 156).

4. NITROSO-β-ALPHYLHYDROXYLAMINES.

 β -Phenylnitrosohydroxylamine, $C_6H_5N(OH)$. NO, melting at 59°, isomeric with diazobenzene acid (see this), is produced when a solution of sodium nitrite acts upon an ice-cold solution of β -phenylhydroxylamine hydrochloride (B. 27, 1548); further, by the action of hydroxylamine and sodium alcoholate upon nitrobenzene (B. 29, 1884). When methylated with diazomethane (1, 207) it yields a methyl ether, C₂H₅N₂O(OCH₂), melting at 38° (B. 29, 2412). sym. Dinitrophenylnitrosohydroxylamine, (NO₂)₂. C₆H₃N(OH)NO, melting at 185°, is obtained from sym. trinitrobenzene and hydroxylamine (B. 29, 2287).

5. AMIDO-COMPOUNDS, OR ANILINES.

These are produced by the substitution of amido-groups for the hydrogen of benzene and alkyl benzenes:

C₆H₅NH₂ Aniline, Amidobenzene

 $C_6H_4(NH_2)_2$ Diamidobenzene

C₈H₃(NH₂)₈ Triamidobenzene.

^{*} Alphyl is an abbreviation for alkylphenyl, $C_2H_{2n+1}C_8H_4$ (Bamberger).

Or, they may be considered as ammonia derivatives, from which might be concluded the existence of primary, secondary, and tertiary amines of the benzene series (p. 77):

 $\begin{array}{ccccc} C_6H_5 \cdot NH_2 & (C_6H_5)_2NH & (C_6H_5)_3N \\ Phenylamine & Diphenylamine & Triphenylamine \\ C_6H_5NH \cdot CH_3 & C_6H_5N(CH_3)_2 \\ Phenylmethylamine & Phenyldimethylamine. \end{array}$

The true analogues of amines of the fatty series—e. g., C₆H₈. CH₁. NH₂, benzylamine—are obtained when the hydrogen of the side-chains is replaced by the amido-group. They will be considered after their corresponding alcohols.

A. PRIMARY PHENYLAMINES.

Formation of primary phenylamines, whose amido-groups are in union with the benzene nucleus:

I. Reduction Reactions.—1. These amido-derivatives are prepared almost exclusively by the reduction of the corresponding nitro-bodies:

$$C_6H_5NO_2 + 6H = C_6H_5NH_2 + 2H_2O.$$

Under suitable conditions the β -phenylhydroxylamines appear as intermediate products of the reduction (p. 65).

The most important methods of reduction are:

(a) The action of ammonium sulphide in alcoholic solution (Zinin, 1842):

$$C_aH_a$$
. $NO_a + 3H_aS = C_aH_a$. $NH_a + 2H_aO + 3S$.

In using this reaction with polynitro-compounds only one nitro-group is reduced, and there result nitroamido-compounds.

In the case of chlornitrobenzenes the nitro-group is only reduced by ammonium sulphide when it is not adjacent to the chlorine or another nitro-group; in the reverse instance sulphur or SH will replace the chlorine or a nitro-group (B. 11, 1156, 2056).

(b) Action of zinc and hydrochloric acid upon the alcoholic solution of nitro-compounds (A. W. Hofmann); or iron filings and acetic or hydrochloric acid (Béchamp, 1852). The latter method (iron and hydrochloric acid) is applied technically in the manufacture of aniline and o- and p-toluidine. The explanation of the course of this reaction will be found under aniline (p. 74).

(c) Action of tin and hydrochloric acid (Roussin) or acetic acid (B. 15, 2105); or a solution of stannous chloride in hydrochloric acid:

$$\begin{array}{ll} C_6H_6 \,.\, NO_9 + 3Sn & +6HCl = C_6H_6 \,.\, NH_2 + 3SnCl_2 + 2H_2O \\ C_6H_6 \,.\, NO_2 + 3SnCl_2 + 6HCl = C_6H_6 \,.\, NH_2 + 3SnCl_4 + 2H_2O. \end{array}$$

This method serves also for the quantitative determination of the nitro-groups. If the alcoholic solution of a polynitro-compound be mixed with an alcohol-hydrochloric acid solution of a calculated quantity of SnCl₂, it will be possible to effect reduction step by step. In the case of o-p-,[2,4]-dinitrotoluene the [4]-NO₂-group will be reduced; whereas, with alcoholic ammonium sulphide it is the [2]-NO₃-group which sustains reduction (B. 19, 2161).

In many instances the following reducing agents have been applied to advantage: (d) Sodium arsenite (J. pr. Ch. [2] 50, 563); (e) Zinc dust in alcoholic or ammoniscal solution; (f) Ferrous sulphate with baryta water (B. 24, 3193), or ammonia (B. 15, 2294), will serve for the reduction of nitro-bodies soluble in water.

2. The reduction of nitroso-compounds—see nitrosobenzene (p. 70) and nitrosodi-

methylaniline (p. 94).
3. Reduction of hydrazo-compounds and hydrazines (see these).
II. Exchange Reactions.—4. The replacement of an halogen atom or of a nitro group, an hydroxyl or alkoxyl group by the amido-group. These reactions have special value in the preparation of substituted primary phenylamines, as the monohaloid derivatives, the mononitro hydrocarbons and phenols only yield traces of the amido-derivatives when heated with ammonia. However, these bodies react the more easily, the greater the number of nitro-groups introduced. [1,2]-Chlor- and bromnitrobenzene, [1,2]-dinitrobenzene, [1,2]-nitrophenol and its alkyl esters, [1,4]-chlor- and bromnitrobenzene, [1,4]-nitrophenol and its esters yield nitroamido-derivatives when heated with ammonia. The [1,3]- or meta-derivatives do not react (B. 21, 1541; A. 174, 276).

Phenols can be directly transformed into primary (and secondary) amines by heating them to 300-350° with ammonia-zinc chloride (ZnCl₂. NH₃) (B. 16, 2812; 17, 2635; 19, 2916; 20, 1254). The naphthols react even more readily:

$$C_{10}H_7$$
. OH + NH₈ $\xrightarrow{ZnCl_2}$ \rightarrow $C_{10}H_7NH_2$ + H_2O
Naphthol
Naphthylamine.

5. By heating the alkali sulphonates with sodamide, NH, Na (B. 19, 902). III. Decomposition Reactions. - 6. By heating amido-carboxylic acids:

$$(NH_2)_2C_6H_3CO_2H = C_6H_4(NH_2)_2 + CO_2$$

Diamidobenzoic Phenylenediamine.

7. By heating secondary and tertiary amines with hydrochloric acid, and when ammonium bases alone are rapidly heated:

$$\begin{array}{l} C_6 II_5 NIICII_3 + HCl = C_6 II_5 \cdot NH_2 + CH_3 Cl \\ C_6 II_5 NIIC_2 II_5 \cdot IIBr = C_6 II_5 \cdot NH_3 + C_2 II_5 Br. \end{array}$$

IV. Nucleus-syntheses.—8. When aniline and methyl chloride are heated some methyl aniline hydrochloride is produced; at higher temperatures this splits into methyl chloride and aniline (see above), and at a still higher temperature (340°) hydrogen in benzene is replaced by methyl and toluidine chlorhydrate is formed. Phenyltrimethyl ammonium iodide yields mesidine hydroiodide:

$$\begin{array}{c} C_6H_5 \\ CH_3 \\ CH_3 \\ \end{array} \\ \text{NII . IICl} \longrightarrow \begin{array}{c} C_6H_4 \cdot \text{NH}_2\text{IICl} \\ CH_3 \\ \end{array} \\ \begin{array}{c} C_6H_5N \\ \end{array} \\ \begin{array}{c} CH_3 \\ CH_3 \\ \end{array} \\ \longrightarrow \begin{array}{c} CH_3 \\ CH_3 \\ \end{array} \\ \longrightarrow \begin{array}{c} C_6H_2(CH_3)_3 \cdot \text{NH}_2\text{HI} \\ \end{array} \\ \begin{array}{c} \text{Phenylmethylamine} \\ \text{Chlorhydrate} \\ \end{array} \\ \begin{array}{c} Chlorhydrate \\ Chlorhydrate \\ \end{array} \\ \begin{array}{c} CH_3 \\ CH_3 \\ \end{array} \\ \longrightarrow \begin{array}{c} CH_3 \\ CH_3 \\ \end{array} \\ \longrightarrow \begin{array}{c} CH_3 \\ CH_3 \\ \end{array} \\ \longrightarrow \begin{array}{c} CH_3 \\ CH_3 \\ \end{array} \\ \begin{array}{c} CH_3 \\ CH_3 \\ \end{array} \\ \longrightarrow \begin{array}{c} CH_3 \\ CH_3 \\ \end{array} \\ \begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ \end{array} \\ \begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ \end{array} \\ \begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ \end{array} \\ \begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ \end{array} \\ \begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ \end{array} \\ \begin{array}{c} CH_3 \\ CH_3 \\ CH_3 \\ CH_3 \\ \end{array} \\ \begin{array}{c} CH_3 \\ CH$$

Secondary and tertiary aromatic bases can be changed to isomeric primary bases in this manner. Instead of the hydrochlorides of the secondary and tertiary bases, salts of primary bases can be heated with suitable alcohols to 300° (B. 13, 1729):

$$\begin{array}{lll} C_6H_5NH_2 . & HCl + C_4H_9OH == C_4H_9 . C_8H_6NH_2 . & HCl + H_9O\\ & & & & & & & \\ Aniline & & & & & & \\ Hydrochloride & & & & & & \\ Hydrochloride & & & & & & \\ Alcohol & & & & & & \\ Hydrochloride & & & & & \\ Alcohol & & & & & \\ Hydrochloride & & \\$$

Or, the free bases can be heated with normal alcohols and zinc chloride to 250° (B. 16, 105).

Such migrations in the nucleus of atomic groups, which replace an hydrogen of the amido-residue of aromatic amines are more frequently observed; compare phenylhydroxylamine, etc. (p. 70); also B. 29, R. 870.

Properties and Transformations of the Phenylamines.—The primary amines are colorless, and have a peculiar but not disagreeable odor. They can be distilled under the ordinary pressure without decomposition. They resemble the alkylamines in their ability to form salts (1, 159); they are, however, much less basic than the primary alkylamines. They do not react alkaline, and dissolve with difficulty in water, although they are volatile with steam.

When negative groups enter the primary phenylamines, they further diminish their basic character; the salts of disubstituted anilines, like C₆H₃Cl₂. NH₂ and C₆H₃(NO₂)₂. NH₂, are decomposed by water, or are not produced.

In chemical behavior they approach the acid amides, just as the oxy-

compounds or phenols possess the character of acids.

Aniline, as the type of primary phenylamines, will be exhaustively studied.

The following are some of the ordinary reactions of the amido-group:

The alkali metals dissolve when heated with the evolution of

1. The alkali metals dissolve, when heated, with the evolution of hydrogen. Aniline affords aniline-potassium, C₆H₆NHK, and aniline-dipotassium, C₆H₆NK₂ (p. 75).

2. The halogen alkyls combine with the anilines, forming secondary,

tertiary, and finally quaternary ammonium derivatives (1, 160).

3. One or two molecules of a primary amine (B. 25, 2020) will unite with a molecule of an aldehyde. Furfurol and all primary anilines yield intensely red-colored bodies.

4. The deportment of the free primary anilines and their salts toward nitrous acid is exceedingly important for the development of the chemistry of the aromatic bodies. The products are diazoamido-bodies and diazo-compounds. The latter are the intermediate steps in the conversion of the nitro- and amido-derivatives into the most varied substitution products.

5. Thionyl chloride converts primary anilines into *thionyl anilines*; this is similar to the behavior of the primary aliphatic amines (1, 165).

6. An hydrogen atom of the amido-group can be very easily replaced by acid residues; the products are acid anilides, corresponding to the acid amides (1, 164). The acet-derivatives crystallize well and are, therefore, very frequently prepared (p. 82).

7. The primary anilines, like the primary aliphatic amines (1, 166),

yield carbylamines with chloroform and caustic potash.

8. The primary anilines and carbon disulphide unite to *dialphylsul-phoureas* with liberation of hydrogen sulphide, whereas the primary aliphatic amines yield *alkyldithiocarbamic acids* (1, 166).

9. The synthesis of quinoline (see this) and other bases containing quinoline nuclei by heating aniline and other primary aromatic bases

with glycerol, sulphuric acid, and nitrobenzene is very suggestive for the development of the chemistry of quinoline. Quinoline derivatives also result in the condensation of fatty aldehydes by means of hydrochloric or sulphuric acid (see quinoline syntheses).

10. Indols are produced on heating primary aromatic bases with a-haloid keto-compounds; sometimes dihydropyrasine derivatives (see these) are also formed.

Aniline, *Phenylamine*, [Aminophene], [Aminobenzene], $C_4H_5NH_5$, melting at -8° , boiling at 184°, with specific gravity 1.0361 at 0°, is an oil with a faint aromatic odor. It dissolves in 31 parts of water at 12.5° (B. 10, 709).

History.—Unverdorben first discovered (1826) aniline in the dry distillation of indigo and called it crystallin, because of the great crystallizing power of its salts. Runge (1834) found it in coal-tar, and named it cyanole, as it gave a blue coloration with a bleaching lime solution. Fritzsche (1841) prepared a base, upon distilling indigo with caustic potash, to which he gave the name aniline, from Indigofera anil, the name of the indigo plant. In the same year (1841) Zinin prepared "benzidam" by the reduction of nitrobenzene with ammonium sulphide. A. W. Hofmann (1843) proved the identity of the four bases (A. 47, 37).

Aniline is made upon a commercial basis by reducing nitrobenzene with iron and about $\frac{1}{40}$ of the quantity of hydrochloric acid required by the following equation:

$$C_6H_5NO_2 + 2Fe + 6HCl = C_6H_5NH_2 + Fe_2Cl_6 + 2H_3O.$$

Probably ferrous chloride is the first product, and in its presence the nitrobenzene is reduced by the iron and water, in that the ferrous chloride acts as carrier. The finely divided metal is the immediate active reducing agent (B. 27, 1436, 1815):

$$C_6H_5NO_2 + 3Fe + 6HCl = C_6H_5NH_3 + 3FeCl_3 + 2H_9O$$

 $C_6H_5NO_2 + 2Fe + 4H_2O = C_6H_5NH_2 + Fe_3(OH)_6$.

The other means of reducing nitrobenzene have already been mentioned on p. 71. In the general methods used in the preparation of primary phenylamines, aniline is usually selected as the example. This is the case in the transformation reactions of the primary phenylamines: action of the alkali metals, halogen alkyls, aldehydes, nitrous acid, thionyl chloride, in the acid anilide formation, in the behavior with carbon disulphide, chloroform, and caustic alkali, glycerol, sulphuric acid, and nitrobenzene, etc. Aniline is quite accessible, and it has been drawn into reactions scarcely less frequently than ammonia itself; consequently we shall frequently encounter it as the parent substance, with numerous aromatic compounds. Despite its feeble basic properties, it will precipitate zinc, aluminium, and ferric salts, and on warming will expel ammonia from its salts. This is because of its slight volatility.

ammonia from its salts. This is because of its slight volatility.

Aniline is poisonous. It is a solvent for many bodies—e. g., indigo.

Aniline is very sensitive to oxidizing agents. In the air it gradually assumes a brown color and resinifies. Bleaching lime imparts a purple color to the solution (B. 27, 3263). On adding sulphuric acid and a few drops of potassium chromate to aniline, a red color appears; later it be-

comes an intense blue. If aniline be oxidized with bleaching lime, aided by heat, or with cold potassium permanganate, it will be changed through a series of intermediate products into *nitrobenzene* (B. 26, 496). Chromic acid converts it into *quinone* (see this), and chlorates in the presence of certain metallic salts change it to *aniline black*.

Aniline is used in the manufacture of numerous technical dyes or compounds with therapeutic value—e. g., aniline black, fuchsine, and

others, as well as of antifebrine, antipyrine, etc., etc.

Aniline Salts.—The hydrochloride is obtained perfectly pure and dry by conducting dry hydrogen chloride into an ethereal solution of aniline. It melts at 192°. In commerce it is known as aniline salt. It deliquesces with water. Platinum Chloride Double Salt yields yellow needles from alcohol. The stannous and stannic salts, SnCl₂. 2C₆H₅NH₂. HCl + 2H₂O and SnCl₄. 2C₆H₅NH₂. HCl + 2H₂O. The sulphate, (C₆H₅NH₂)₂SO₆H₂. The nitrate crystallizes in large rhombic plates; the oxalate forms rhombic prisms. Not only the hydrochloride, but also free aniline combines with certain salts to form double salts. It forms an additive compound with trinitrobenzene (p. 67).

Aniline-potassium, C₈H₈NHK and C₆H₈NK₂. They are not known in a pure state. The formation of di- and triphenylamine in the action of brombenzene upon the reaction product resulting from aniline and potassium proves that the hydrogen of the amido-group has been replaced by potassium. Sodium first begins to act upon aniline at

200°; compare further acetanilide (p. 82) and monomethylaniline (p. 78).

Amidomethyl Benzenes.—Some representatives of this group are of the first importance in the color industry. This is particularly true of o- and p-toluidine. Most of the bases are liquids at the ordinary temperatures, but when boiled with glacial acetic acid, with acetyl chloride, or acetic anhydride they readily yield acet-derivatives (p. 82). These substituted acetamides crystallize well, have definite melting points, and are in every way well suited for the recognition of the bases, from which they can be obtained in a very simple way. Therefore, the melting point of the acet-derivative will, in the future, always be given with the boiling point and melting point of the base. The amidomethyl benzenes are made by the reduction of the corresponding nitro-bodies, and by heating under pressure at high temperatures the hydrochlorides of bases which have the methyl groups in union with nitrogen—e.g., dimethylaniline, $C_eH_bN(CH_b)_2$.

Toluidines, CH₃. C₆H₄. NH₃. The three toluidines are isomeric with benzylamine, C₆H₅. CH₂. NH₄ (treated after benzyl alcohol), and with methylaniline, C₆H₅NH. CH₃ (p. 78). They are made by the reduction of the three nitrotoluenes (p. 68). m-Toluidine is also formed by the reduction of m-nitrobenzal chloride, a transposition product of m-nitrobenzaldehyde (B. 15, 2009; 18, 3398). A. W. Hofmann and Muspratt

discovered p-toluidine in 1845 (A. 54, 1).

o-Toluidine, liquid, boils at 197°; Acet-o-toluide melts at 110° and boils at 296°.

m-Toluidine, liquid, boils at 199°; Acet-m-toluide melts at 65° and

p-Toluidine, m. p. 45°, boils at 198°; Acet-p-toluide melts at 153° and boils at 307°.

Separation of o- and p-Toluidine.—The nitration of toluene produces o- and p-nitrotoluene; these, by reduction, yield the toluidines, very valuable in the technical way.

o-Toluidine is separated from the p-toluidine by treating the mixture of bases with a quantity of sulphuric acid insufficient to fully neutralize them and then distilling. The stronger p-base remains as sulphate. Or, the greater solubility of the o-toluidine oxalate (J. pr. Ch. [2] 14, 449), as well as o acet toluide (B. 2, 433) is used for separation from the corresponding p-bodies. Aniline, ortho- and para-toluidine can also be separated by the varying behavior of their hydrochlorides toward monosodium phosphate (B. 19, 1718, 2728; B 29, R. 434).

In the chemistry of aniline colors the following distinctions are made:

Aniline Oil for Blue: pure aniline;
Aniline Oil for Red: molecular quantities of aniline, o- and p-toluidine;

Aniline Oil for Safranine: aniline and o-toluidine, obtained from the distillate (échappés) of the fuchsine fusion.

The free toluidines are easily converted by oxidation into azo-compounds (B. 26, 2772). If the amido-group be protected from oxidation by the introduction of an acid radical,—e. g., the acetyl group,—the methyl group can be oxidized to carboxyl by means of potassium permanganate; thus, o-acet toluide will yield o-acet-amidobenzoic acid (B. 14. 263). In the chlorination, bromination, or nitration of the acet toluides, the negative substituent usually adds itself in the o-position to the acetamido-group (compare m-nitrotoluene, p. 68).

Bleaching lime and hydrochloric acid color o-toluidine, like aniline, violet; p-toluidine is not thus affected. Ferric chloride precipitates a blue compound, toluidine blue, from the solution of o-toluidine hydrochloride.

Xylidines, (CH₃)₂C₆H₃NH₂. The six possible isomerides are known:

```
v-o-Xylidine, liquid,
                               boils at 223°; corresponding Acetxylide, m. p. 134°.
                                 " " 226°;
unsym.-o-Xylidine, melts at 49°,
                                                                            99°.
                                    " 216°;
                                 "
                                                   "
                                                               "
                                                                       "
     v-m-Xylidine, liquid,
                                 "
                                    " 212°;
                                                   "
                                                               "
                                                                       "
unsym:-m-Xylidine, "
                                                                            1 20°.
                                    " 220°;
  sym.-m-Xylidine,
                    "
                                 "
                                                   46
                                                               "
                                                                       66
                                                                            144°.
       p Xylidine, melts at 15°,
                                 "
                                    " 213°;
                                                               "
                                                                            180°.
```

The xylidine obtained from dimethyl aniline and serving in the manufacture of dyes

consists mainly of unsym.-m-xylidine and p-xylidine (B. 18, 2664, 2919).

Amidopolymethyl Benzenes, (CH₃)₃C₆H₂NH₂. The product obtained technically by heating xylidine hydrochloride with methyl alcohol to 250°, under pressure, consists principally of s-pseudocumidine and mesidine. It is used in preparing red azo-dyes (B. 15, 1011, 2895).

sym. Pseudocumidine, [5NH₃,1,2,4], melts at 68° and boils at 235°; its acet-de-

rivative melts at 164° (B. 18, 92, 2661).

Mesidine, [2NH₂,1,3,5], liquid, boils at 230°; acet-derivative melts at 216° (B. 18, 2229; 24, 3546).

Isoduridine, [4NH,1,2,3,5], melts at 23° and boils at 255°; its acet-derivative melts at 215° (B. 18, 1149).

Prehnidine, [5NH2,1,2,3,4], melts at 64° and boils at 260°; its acet-derivative melts at 170° (B. 21, 644, 905).

Amidopentamethyl Benzene melts at 151° and boils at 277°; the acet-derivative

melts at 213° (B. 18, 1825).

Homologues of Aniline with Larger Alcohol Radicals.—These have been prepared not only by reduction of the corresponding nitro-compounds, but also by a nucleussynthesis from aniline itself, by heating aniline together with fatty alcohols and zinc chloride to 250-280° (p. 72). The alkyl assumes the p-position with reference to the amidogroup. If isobutyl and isoamyl alcohol be used, then p-tertiary butyl- and p-tertiary

كمد

amyl aniline are produced (B. 28, 407). If phenol be substituted for aniline in this synthesis, the corresponding phenols (see these) will be produced.

p-Amidoethyl benzene, C₂H₅C₆H₄NH₃, melts at —5° and boils at 216° (B. 22, 1847). p Amidopropyl benzene boils at 225°; the acet-derivative melts at 87° (B. 17, 1221). p-Amidoisopropyl benzene boils at 225°; the acet-body melts at 102° (B. 21, 1159). p-Amidotertiarybutyl benzene melts at 17° and boils at 240°; the acet-body melts at 172° (B. 24, 2974).

p-Amido-octyl bensene melts at 19° and boils at 310°; the acet-derivative melts at 93°

(B. 18, 135).

B. SECONDARY AND TERTIARY PHENYLAMINES. PHENYLAMMONIUM BASES.

Phenylalkylamines.—Formation: (1) The alkyl anilines and homologues of aniline are formed the same as the amines of the fatty series (1, 160) by the action of alkyl bromides and iodides upon primary bases. They can also reactions usually take place at the ordinary temperatures. be obtained by heating aniline hydrochloride, or, better, aniline hydrobromide (B. 19, 1939), to 250° with alcohols. Alkyl chlorides or bromides are first produced, but they subsequently act upon (2) According to method (1) haloid salts of the monoand dialkyl anilines are formed side by side. To prepare the monoalkyl anilines it is advisable to start with the acet-derivatives of the primary bases, which are dissolved in toluene or xylene, and the calculated amount of metallic sodium is then introduced into the solution. There is an evolution of hydrogen, and white, solid sodium acetanilide separates. This rearranges itself very readily with the alkyl iodides. Saponification of the alkyl acetanilide liberates the alkyl aniline:

$$C_6H_5N{<_H^{CO\cdot CH_3}} \xrightarrow{Na} C_6H_5N{<_{Na}^{CO\cdot CH_3}} \xrightarrow{CH_5I} C_6H_5N{<_{CH_3}^{CO\cdot CH_3}} \xrightarrow{>} C_6H_5N{<_{CH_3}^{II}}$$

Separation of Primary, Secondary, and Tertiary Bases.—Sodium nitrite precipitates the secondary bases as oily nitrosamines from an acid solution of a mixture of the same. The bases are regained by treating the nitrosamines with tin and hydrochloric acid. The ferrocyanide salts (A. 190, 184) or the metaphosphates will also answer for this purpose (B. 10, 795; 22, 1005; 26, 1020).

Phenylalkylammonium Bases.—Tertiary phenylalkylamines—e.g., $C_0H_0N(C_2H_0)$,—are capable of uniting with the alkylogens to ammonium derivatives, which moist silver oxide or lime converts into ammonium hydroxides: $C_0H_0N(C_2H_0)$, I yields $C_0H_0N(C_2H_0)$.

 $(C_{\bullet}H_{\bullet})_{\bullet}OH.$

Properties and Transpositions.—The most important bodies in this group are the methyl and ethyl anilines. When freshly prepared, they are colorless, strongly refracting liquids, which slowly turn brown on exposure to light. Their odor is similar to, but more agreeable than, that of aniline.

The secondary phenylalkylamines recall in their deportment the dialkylamines (1, 167). (1) They form salts and combine with alkylogens to haloid salts of the tertiary amines. (2) Acid chlorides and acid anhydrides substitute acid radicals for the imide hydrogen. The same compounds can also be obtained in the manner outlined in method 2.

(3) Nitrous acid converts them into nitrosamines (1, 170).

The tertiary phenyldialkylamines, containing an aromatic hydro-

gen atom in the para-position with reference to the dialkylamido-group, show a remarkable mobility of this atom of hydrogen, permitting a series of reactions for which the primary and secondary anilines are not adapted, or at least not to so great a degree. The behavior of the phenyldialkylamines toward nitrous acid is particularly important, both theoretically and technically. It converts them into p-nitroso-derivatives.

The three classes of aromatic amines differ therefore from each other in their deportment toward nitrous acid, as follows:

1. Primary phenylamines yield diazo-derivatives or diazoamido-com-pounds.

2. Secondary phenylalkylamines yield nitrosamines.

3. Tertiary phenyldialkylamines yield p-nitroso-compounds.

Other reactions of the phenyldialkylamines will be mentioned after discussing dimethyl aniline.

The methyl- and ethyl-anilines have the following melting points and

specific gravities:

Monomethyl Aniline, liquid, boils at 192°; sp. gravity, 0.976(15°). Dimethyl Aniline melts at 0.5°, and boils at 192°; sp. gravity, 0.9575 (20°/4°).

Ethyl Aniline, liquid, boils at 206°; sp. gravity, 0.954 (18°).
Diethyl Aniline, liquid, boils at 213.5°; sp. gravity, 0.939 (18°).

The methylated anilines are technically applied in the production of aniline dye-stuffs. They are formed on heating aniline together with HCl-aniline and methyl alcohol to 220°. A better course is to conduct CH₃Cl into boiling aniline.

Methyl Aniline, C₆H₆. NH(CH₃), is obtained from phenyl carbylamine (p. 83). Its salts (with HCl and H₂SO₄) do not crystallize and dissolve in ether (distinction from the corresponding aniline salts, which are insoluble in this solvent). Bleaching lime imparts no color to it. When methyl aniline is heated to 330°, it is transformed into paratoluidine, C₆H₄(CH₃). NH₂. Methylphenylnitrosamine, see p. 97. Methylacetanilide, see p. 82.

Dimethyl Aniline, C₆H₅. N(CH₃)₂. Its salts do not crystallize. It forms an acetate; this decomposes again into its components on distillation. Hypochlorites do not color it. It forms trimethylphenylium

iodide, C₆H₅. N(CH₃)₃I, with methyl iodide.

The action of nitrous acid or, better, sodium nitrite upon the HCl-salt produces p-Nitroso-dimethyl Aniline.

p Nitro-dimethyl Aniline is obtained with nitric acid.

Benzoyl chloride and acetyl bromide convert it into benzoyl and acetyl monomethyl

aniline, together with trimethylphenylium bromide (B. 19, 1947).

Dimethyl aniline has been introduced into a series of condensation reactions. It combines to p-amidomandelic acid, (CH₃)₂N[4]C₆H₄[1]CH(OH). CCl₃, with chloral. Phosgene converts it into tetramethyl-p-diamidobensophenone, [(CH₃)₂N[4]C₆H₄[1]]₂CO, while with orthoformic ester and zinc chloride it yields hexamethyl-p-leucaniline, CH-[C₆H₄N(CH₃)₃], and with benzotrichloride malachite green (see this), etc.

 $[C_6H_4N(CH_3)_2]_3$, and with benzotrichloride malachite green (see this), etc.

The homologous mono- and dialkyl anilines behave similarly. Mention may also be made of methylethyl aniline, $C_6H_5N(CH_3)(C_2H_5)$, boiling at 201°. Its compound with CH_3I is identical with dimethyl-aniline-ethyl iodide; methyl-ethyl aniline-ethyl

iodide is also identical with diethyl aniline-methyl iodide; finally, methyl-propyl anilineethyl iodide is identical with ethyl-propyl aniline-methyl iodide—an additional proof that the five affinities of nitrogen have equal value (1, 169 and B. 19, 2785). The higher alkyl is set free from all these ammonium iodides when they are heated with caustic pot-

Alkylen-dianilines: Methylene-diphenyl-diamine, $CH_2(NHC_6H_5)_2$, melting at 65°, is formed from aniline and formaldehyde in alkaline solution, as well as upon heating anhydroformaldehyde-aniline (see below) to 100° with alcoholic aniline (B. 27, Hydrochloric acid or aniline hydrochloride rearranges it to diamido-diphenyl methane (compare the bensidine rearrangement):

$$CH_{2}(NHC_{4}H_{5})_{2} = CH_{2}(C_{4}H_{4}.NH_{2})_{2}.$$

Ethylene Diphenyl-diamine, (C₈H₅. NH)₂C₂H₄, from aniline and ethylene bromide, melts at 65°.

Ethylene Monophenyl-diamine, NH₂.CH₂.CH₃.NH.C₆H₅, boiling at 263°,

has been prepared by means of potassium phthalimide (B. 24, 2191).

Ethylene Isobutylidene-diphenyl-diamine, $CH_2 \cdot N(C_6H_5) > CH \cdot C_3H_7$, melting at 250 and 5 from at bloodish and the contract of the

ing at 95°, results from ethylenediphenyldiamine and isobutylaldehyde. Diethylenediphenyldiamine, n-diphenylpiperazine; see piperazine.

Alkylidene Anilines.—These are produced in energetic reactions by the union of fatty aldehydes and aniline. An exit of water occurs. The simple bodies are usually unstable oils, which immediately polymerize in part like formaldehyde-aniline, or partly condense in an aldol-like manner. The simple and polymeric alkylidene anilines readily absorb hydrocyanic acid and form nitriles of the a-anilido-acids. Those

having an aidol nature do not behave in this way; they readily condense, with exit of aniline, to quinoline derivatives (see *quinaldine* syntheses) (B. 25, 2020).

Anhydroformaldehyde Aniline, (CH₂NC₄H₆)₃, melting at 140°, has been prepared by mixing a solution of well-cooled formaldehyde with aniline. It yields methyl aniline

upon reduction, and anilido-acetonitrile with prussic acid.

Ethidene Aniline, CH_3 . $CH: N. C_6H_5$, is an oil. It absorbs hydrocyanic acid readily and condenses, without difficulty, to two modifications of β -anilidobutylidene-aniline, CH_3 . $CH(NH . C_6H_5)CH_3$. $CH: N. C_6H_5$, melting at 126° and at 85°. The latter can be rearranged into the former or high melting body. When heated with hydrochloric or acetic acid they yield quinaldine, while nitrous acid changes them to two dinitroso-compounds, melting at 161° and 120° (B. 29, 2977). Aldol-aniline, CH, CH(OH)CH, CH: N.C₆H₅, from aldol and aniline, is a reddish-colored and easily decomposable oil. Ammonium sulphide changes it to thioaldol aniline, CH_3 . CH(OH). CH_2 . CH S N. C_6H_6 , melting at 92° (B. 29, 59).

C. Polyphenylamines.—The methods of producing these bodies and their behavior will be explained in connection with diphenylamine and triphenylamine.

Diphenylamine, NH(C₆H₅)₂, melts at 54° and boils at 310°.

1. This compound is very important from a technical standpoint. was prepared by A. W. Hofmann (1864) on heating aniline blue, rosaniline, and similar dye-substances (A. 132, 160).

2. It is made by heating aniline hydrochloride and aniline to 240°:

$$C_{a}H_{5}$$
. NH_{4} . $HCl + C_{a}H_{5}$. $NH_{4} = (C_{a}H_{5})_{4}NH + NH_{4}Cl$.

The homologous *ditolylamines* have been similarly obtained.

3. It results also upon heating aniline with phenol and ZnCl, to 260°.

4. It is, furthermore, formed when brombenzene and aniline are heated to 350-390° together with soda-lime (B. 27, R. 74).

Diphenylamine is a pleasant-smelling, crystalline compound. almost insoluble in water, but readily soluble in alcohol and ether. a very weak base, whose salts are decomposed by water.

Potassium permanganate, in alkaline solution, oxidizes diphenylamine to diphenylp-azophenylene or quinone-dianil, C₆H₄ { [1]N.C₆H₆, (4]N.C₆H₆. Chlorine and bromine convert it into tetra- or hexa-halogen substitution products, and nitric acid changes it to the hexanitro derivative (p. 93). Sulphuric acid dissolves diphenylamine; the solution has a dark-blue color when traces of nitric acid are present : test for nitric acid.

Nitrodiphenylamines (see p. 93).—Nitrosdiphenylamine (p. 94). On heating diphenylamine with sulphur it yields thiodiphenylamine, NH $< \frac{C_0}{C_0} \frac{H_0}{H_0} > S$ (see this), the parent substance of the thionine dyes. Acridines—e.g., $N = \frac{C_0}{C_0} \frac{H_0}{H_0} > CH$ —are produced—then is in heated to 2009 with fatty saids. Diphenylamine is applied in the

duced when it is heated to 300° with fatty acids. Diphenylamine is applied in the manufacture of triphenylrosaniline (see this) or aniline blue. Methyl Diphenylamine, $CH_2N(C_2H_5)_2$, boils at 292° (A. 235, 21).

Triphenylamine, (C₆H₅)₃N, is obtained on heating dipotassium aniline (p. 75) or sodium diphenylamine with brombenzene (B. 18, 2156). It crystallizes from ether in large plates, melts at 127° and distils undecomposed. It dissolves in sulphuric acid, forming a violet, then a dark-green color. It cannot form salts with acids. By nitration it yields a trinitro-product, which forms triamidotriphenylamine, N(C₆H₄. NH₂)₃, Hexaphenylrosaniline is produced when by reduction (B. 19, 759). phosgene acts upon triphenylamine.

ANILINE DERIVATIVES OF INORGANIC ACIDS.

Aromatic Thionylamines (Michaelis).—These bodies, corresponding to the alkylthionylamines (1, 165), are produced when thionyl chloride acts upon primary bases. This reaction is characteristic of these derivatives. The thionylamines are mostly yellowcolored liquids, boiling at the ordinary pressure without decomposition. They have a peculiar aromatic odor; at the same time the odor of sulphur chloride.

Thionyl Aniline, C₆H₅N: SO, boils at 200° and has the specific gravity 1.236 (15°). Thionyl-o-chloraniline boils at 207° under 46 mm. pressure; the m-body boils at 233°, and the p-compound melts at 36° and boils at 237°. Thionyl-o-bromaniline boils at 210° under 46 mm. pressure; the m-body melts at 32° and the para- at 60°. Thionyl-o-nitraniline melts at 32°.

Thionyl-o-toluidine boils at 1840 under 100 mm. pressure; the m-compound boils

at 220°, while the p derivative melts at 7° and boils at 224° (A. 274, 201), etc.

Phenylsulphamic Acid, C₆H₅NHSO₃H, only known in the form of salts, is produced when SO₃ or CISO₃H acts upon aniline dissolved in chloroform (B. 24, 360), as well as by heating aniline with amidosulphonic acid (B. 27, 1244). p. Tolylsulphamic Acid is precipitated from its ammonium salt solution by acids (B. 28, 3161). Sulphanilide, $SO_2(NHC_6H_5)_2$ (B. 24, 362).

The aromatic nitrosamines and nitroamines will be discussed later, before the

diazo-derivatives.

Phosphorphenylamines.—Phosphazobenzene Chloride, CallaN: PCl, melting at 136-137°, was made by allowing PCl₃ to act upon aniline hydrochloride. Phenol changes it to *Phenoxylphosphasobenzene*, C₆H₅N: P(O. C₆H₅), while with aniline it forms phosphasobenzene anilide, C₆H₅N: P. NH. C₆H₅ (B. 27, 490). Anilido-phosphoric Dichloride, C₆H₅NH. POCl₃, melting at 84°, can be prepared from POCl₃ and aniline hydrochloride (B. 26, 2939). Orthophosphor-anilide, (C₆H₅NH)₅PO, melts at 208° (A. 229, 334). Oxyphosphasobenzene anilide, C₆H₅NH. PO: N. C₆H₅, melting at 357°, is the final product in the action of POCl₃ upon aniline (B. 29, 716). *Trichlorphosphanil*, C₆H₅N. PCl₃ (B. 28, 2212), is formed from aniline hydrochoride and phosphorus pentachloride.

Sulphophosphazobensene chloride, CaH5N: PSCI, melting at 149° and boiling at 280-

290°, is formed from PSCl₂ and aniline hydrochloride (B. 28, 1239).

Arsenphenylamines are produced in the action of arsenious chloride or bromide upon aniline dissolved in ether or chloroform. Arsenanilido-dichloride, C₆H₅NHAs-Cl₂, melts at 87°. Arsenanilido-dibromide melts at 112°. Arsendianilido-mono-chloride, (C₆H₅NH)₂AsCl, melts at 127°. Arsenanilido-dimethyl Ether, C₆H₅-NHAs(OCH₃)₂, boils at 55° under 12 mm. pressure (A. 261, 279).

Silicotetraphenylamide, Si(NHC₆H₅), melts at 137° (B. 22, R. 746).

CARBONIC ACID DERIVATIVES OF THE AROMATIC PRIMARY AND SECOND-ARY AMINES.

In the introduction to the fatty acids an example was given in connection with acetic acid to show what nitrogen-containing derivatives could be obtained by changes in the carboxyl group (1, 222). The first category contained the acid amides, which may be variously constructed, corresponding to the formulas—

The imidoethers are derived from the second formula.

Numerous fatty acid derivatives of these classes have been obtained from aniline and its primary homologues. With acid amides of secondary bases only, formula 1 comes into consideration. In a primary amine both hydrogen atoms are replaceable by acid radicals.

The thiamides and isothiamides correspond to the acid amides:

The amide chlorides, imide chlorides, and the amidines attach themselves to these classes.

Anilides of Monobasic Fatty Acids.—The anilides or phenylamides of the fatty acids are made by the methods given for the acid amides (1, 262):

(1) By heating the aniline salts of the fatty acids. (2) By the action of aniline upon esters, (3) upon acid chlorides, and (4) upon acid

anhydrides.

The acid anilides are very stable derivatives; can usually be distilled without change, and also directly chlorinated, brominated, and nitrated (p. 77). They furnish a rapid and simple means of distinguishing the aromatic bases. They are resolved into their components by digesting them with alkalies or heating with hydrochloric acid. They yield benzothiazoles when they are heated with sulphur.

The secondary anilides, like secondary alkyl anilines (p. 97), yield nitrosamines by the action of nitrous acid.

These give the nitrosamine reaction with phenol and sulphuric acid; but are less stable than the nitrosamines of the secondary anilines. Reducing agents break off

their nitroso-group. The anilides of formic and acetic acids will be described in the following paragraphs:

Formanilide, C₈H₅. NH. CHO, is obtained on digesting aniline with formic acid,

or by rapidly heating it together with oxalic acid.

It is readily soluble in water, alcohol, and ether. It melts at 46° and boils at 284°,

with scarcely any decomposition.

Salts and Alkyl Derivatives. - Concentrated sodium hydroxide precipitates the crystalline compound, CaHo NNa, Sodium Formanilide, which methyl iodide changes to methyl formanilide, melting at 12.5° and boiling at 253°. The latter is resolved into acid and methyl aniline when it is digested with alcoholic potash or hydrochloric acid (B. 21, 1107). Silver nitrate added to the alcoholic solution of the sodium compound precipitates silver formanilide, C₆H₅. N:CH(OAg). Methyl iodide converts the latter into methyl isoformanilide, C₆H₅. N:CH.O.CH₃, boiling at 196° (B. 23, 2274; R. 659). However, the silver salt and acid chlorides—e. g., benzoyl chloride—yield N-derivatives (B. 29, R. 1141). Ethyl Isoformanilide, ethoxymethylene aniline, C₆H₅N:CH(O₂H₅, boiling at 212°, is obtained, together with diphenylformamidine, by the prolonged boiling of aniline with orthoformic ester (A. 287, 260). Phenylimidethe prolonged boiling of aniline with orthoformic ester (A. 287, 360). Phenylimideformylchloride hydrochloride, $(C_6H_5N=C<\frac{H}{C_1})_2HCl$, is produced when dry hydrochloric acid gas is conducted into an ethereal solution of phenylisocyanide (p. 83) (A. 270, 303).

Acetanilide, Antifebrine, C. H. NH. CO. CH., melting at 112° and boiling at 304°, is produced on boiling aniline with glacial acetic acid (B. 15, 1977) (for the speed of the reaction consult J. pr. Ch. [2] 26, 208), or from aniline and acetyl chloride or acetic anhydride, as well as from malonanilic acid (p. 91). Its formation on heating isomeric acetophenone-oxime to 100° with sulphuric acid is especially noteworthy (B. 20, 2581):

 $C_eH_aC = (NOH) \cdot CH_a \longrightarrow C_eH_aNH \cdot CO \cdot CH_a$

Acetanilide crystallized from water, in which it is sparingly soluble in the cold, consists of small white leaflets. It is used as an antipyretic and antirheumatic. Consult A. 184, 86, for the action of PCls. Bisthiazole (see this) is formed when it is heated with sulphur.

Salts.—Its hydrochloride is decomposed by water. When it is heated it yields diphenyl ethenylamidine, flavaniline (see this), and dimethyl quinoline (B. 18, 1340). Ethylaniline, together with acetic acid, is the product on heating acetanilide with sodium

alcoholate (B. 19, R. 680).

Sodium Acetanilide, CaHaNNa. COCHa, obtained by the action of sodium upon acetanilide dissolved in xylene, is changed by alkyl iodides into monoalkylacetanilides (B. 10, 328), from which the monoalkylanilines can be obtained (B. 23, 2587). same acetanilides are produced when acetic anhydride acts upon secondary bases. Mercurio-acetanilide, (C₈H₅NCO. CH₃)₃Hg (B. 28, R. 113).

Methyl Acetanilide, Exalgine, melts at 101° and boils at 253° (antineuralgic).

Ethyl Acetanilide melts at 54° and boils at 258°.

n-Propyl Acetanilide melts at 47° and boils at 266° (B. 21, 1108).

Substituted Acetanilides.—o- and p-Derivatives of acetanilide are obtained by the action of chlorine, bromine, and nitric acid (p. 92).

Formyl Acetanilide, C₆H₅N(COH)(COCH₂), from mercurio-formanilide and acetyl

chloride, melts at 56° (B. 29, R. 1155).

Diacetanilide, C_eH₅N(CO. CH₃)₂, melting at 37° and boiling at 142° under 11 mm.

pressure, results when acetanilide is heated to 170-180° with acetyl chloride or with acetic anhydride to 200°, as well as upon boiling phenyl mustard oil with acetic anhydride (B. 27, 91; 28, 1665).

The acet-derivatives are characterized by their great power of crystal-They serve as a means of detecting many primary and secondary aromatic bases. Therefore the melting points of many acet-bodies will be introduced in connection with their respective bases (p. 76).

Nitroso-anilides, see p. 97.

Thioanilides result upon treating the anilides with P2S5, and the amidines and iso-

nitriles with H.S.

Thioformanilide, CaHa. NH. CHS, melts at 137° and decomposes at the same time into H₂S and phenyl isocyanide (B. 11, 338; A. 192, 85). Consult B. 18, 2292, upon homologous thioformanilides.

Thioacetanilide melts at 75°. An alkaline solution of potassium ferricyanide oxidizes it to ethenyl amido-thiophenol, C₆H₄ $\stackrel{N}{\sim}$ C. CH₃ (B. 19, 1072).

Methyl-thioacetanilide melts at 58-59° and boils at 290°.

Methyl-isothioacetanilide, C₈H₈N: C<CH₃, boiling at 245°, and Ethyl-isothioacetanilide, boiling at 250°, are obtained by the action of sodium alcoholate and alkyl iodides upon thioacetanilide (similar to formation of phenyl-isothio-urethanes, p. 86, and of phenyl-isothio-ureas, p. 87).

They decompose into aniline hydrochloride and thioacetic ester, CH₃. CO. SR, when

shaken with hydrochloric acid (B. 12, 1061).

Phenylated Amidines of Formic Acid and Acetic Acid.—In addition to the methods proposed for the formation of amidines, the phenylated amidines are produced by the action of PCl₃ or hydrochloric acid upon a mixture of aniline and anilide, when an exit of water occurs (B. 15, 208, 2449):

$$C_{\textbf{6}}H_{\textbf{5}}NHCOCH_{\textbf{3}}+C_{\textbf{6}}H_{\textbf{6}}NH_{\textbf{2}}=\frac{C_{\textbf{6}}H_{\textbf{6}}NH}{C_{\textbf{6}}H_{\textbf{5}}N}C.CH_{\textbf{3}}+H_{\textbf{2}}O.$$

They are feeble bases, and form salts with one equivalent of hydrochloric acid. They

break down into aniline and acid anilides when boiled with alcohol.

Diphenyl-formamidine, Methenyl-diphenyl diamine, C6H5N: CH. NH. C6H5, melting at 135°, results upon heating aniline with chloroform or formic acid to 180°, and by boiling phenyl-isocyanide, C₆H₆. NC, with aniline. It crystallizes from alcohol in long needles and distils at 250°, with partial decomposition, into benzonitrile and aniline. Diphenyl-ethenyl-amidine melts at 131°.

Phenyl-ethenyl-amidine, C₈H₅N: C(NH₂). CH₃, from acetonitrile and HCl-ani-

line (A. 184, 362; 192, 25) (1, 261), is a liquid.

Phenylisuretine, C. H. NH. CH: NOH, melting with decomposition at 138°, has

been obtained from formylchloride-oxime (1, 233) and aniline (B. 27, R. 745).

Phenylated Carbylamines (1, 236).—Phenyl isocyanide, Phenyl carbylamine, C₆H₆N: C, boils under ordinary pressure at 166° (when polymerization occurs) and unaltered at 64° under a pressure of 20 mm. The colorless liquid soon acquires a clear blue, and finally a dark blue, color, when it resinifies. Its sp. gravity at 15° equals 0.977. Phenyl isocyanide is produced by the action of chloroform on aniline in an alcoholic solution of caustic potash, or by the distillation of thioformanilide (above). It has an exceedingly disagreeable and permanent odor, a bitter taste, and increases the flow of saliva and produces headache.

It behaves as follows: (1) When heated to 220° it is rearranged into benzonitrile, C₈H₅CN. (2) Nascent hydrogen converts it into methyl aniline. (3) Hydrochloric acid, in dry ether, changes it to phenylimidoformyl chloride (p. 82); with (4) glacial acetic acid it yields formanilide; with (5) hydrogen sulphide at 100°, thioformanilide; (6) with sulphur at 130°, mustard oil; (7) with aniline at 170°, diphenyl formanilide; (8) with chlorine, isocyanphenyl chloride or phenylimidocarbonyl chloride (p. 89); (9) with phosgene, mesoxanilimide chloride, C₆H₅N = CCl. CO. CCl = N. C₆H₅; (10) with acetyl chloride, pyroracemic anilide (Nef, A. 270, 274). o-Tolylisocyanide boils at 15° (16 mm); an gravity 0.068 at 24°. P. Tolylisocyanide boils isocyanide boils at 75° (16 mm.); sp. gravity 0.968 at 24°. p-Tolylisocyanide boils at 99° (32 mm.) (B. 27, R. 792).

Phenylamine Derivatives of Oxy-acids.—These compounds are well adapted for certain condensations in which the benzene hydrogen holding the ortho-position with reference to nitrogen takes part, so that a heterocyclic derivative results. The acids are obtained by heating the corresponding haloid fatty acids with aniline. The nitriles are produced by adding prussic acid to the alkylidene anilines (p. 79), or by heating the aldehyde cyanhydrins with aniline.

Anilido-acetic Acid, Phenyl glycocoll, Phenylglycin, is obtained from chloror brom acetic acid by the action of aniline and water (B. 10, 2046; 21, R. 136). It

melts at 127°.

Its alkyl esters are produced when aniline is heated with the diazo-acetic esters. Its nitrile, from anhydroformaldehyde aniline and absolute prussic acid, melts at 43°. If the free acid be heated to 150°, it passes into diphenylglycin anhydride or diphenyl-

diacipiperazine, melting at 263° (B. 25, 2270).

In addition to phenylglycin, aniline and chloracetic acid yield diglycolphenylamidic acid, $C_6H_5N(CH_2\cdot CO_2H)_2$, melting at 150-155° (B. 23, 1990). Its anhydride, $C_6H_5\cdot CO_2H_2\cdot CO_3$ (B. 26, 2272). The imide, $C_6H_5N(CH_2\cdot CO_3)$ (B. 26, 1802). The anil, $C_6H_5N(CH_2\cdot CO_3)$ (B. 22, 1802). When phenylglycin and bromacetanilide, C_6H_5NH . CO. CH₂Br, melting at 131°, are fused with caustic potash in the air, indigo results. The distillation of a mixture of calcium anilido-acetate and formate produces indol, $C_6H_6 \times C_6H_6 \times C_6H_6$

Thiodiglycol-anilic Acid and Anilide (A. 273, 70).

- o Nitrophenylglycin, NO₂[2]C₆H₄[1]NH.CH₂.CO₂H, melts at 193° (see quinoxalines).
- a-Anilidopropionic Acid, *Phenylalanine*, C₆H₅NHCH < CO₂H CH₃, melting at 162°, has been prepared from its nitrile, the rearrangement product arising from ethidene cyanhydrin and aniline, as well as from ethidene aniline and prussic acid (B. 15, 2036; 23, 2010; 25, 2032). β-Anilidopropionic Ester, from β-iodpropionic ester, boils at 175° (18 mm.) (B. 29, 514).

Aniline Derivatives of Ketone Carboxylic Acids.—Pyroracemic Anilide, CH₃, CO, CO, NH, C₆H₅, melts at 104°. Pyroracemic Anilide Chloride, CH₃, CO, CCl: N, C₆H₅, boiling at 136° (13 mm.), is prepared from phenyl carbylamine and acetyl chloride (A.

270, 299).

Anil-pyroracemic Acid, C₆H₅. N: C(CII₅). CO₂H, melting, with decomposition, at 122°, is formed from pyroracemic acid and aniline dissolved in ether (A. 263, 126). It changes readily into anil-uvitonic acid, a derivative of quinoline.

By heating aniline and acetoacetic ester to 130° Acetoacetanilide, CH₂ < CO · CH₃ CO · NH · C₆H₅, is produced. It melts at 85°. It condenses to γ-methyl carbostyril.

When aniline and acetoacetic ester interact at the ordinary temperature, there is formed anil-acetoacetic ester, that may be considered as β -Phenylimido-butyric **Ester**, CH_1 , $C(NH, C_0H_0)$: CH, CO₂, R, or β -Anilido-crotonic **Ester**, C_0H_0N -

H.CCCH. CO.R. This is a thick oil, boiling without decomposition under 12 mm. pressure. Acids and alkalies decompose it into its components. It condenses to γ-oxyquinaldine (see this) and phenyl lutidon-carboxylic acid (B. 20, 947 and 1398; 22, 83). The tolylamido-derivatives behave similarly (B. 21, 523).

ANILINE DERIVATIVES OF CARBONIC ACID.

The compounds belonging in this class are very numerous, and will be treated in the order observed with the amine and alkylamine derivatives of carbonic acid, with which

they can thus be most satisfactorily compared (see vol. 1).

Carbanilic Acid, phenyl carbamic acid, is not known in a free state. Its esters, called phenyl urethanes, result (1) in the action of chlorcarbonic esters upon aniline (B. 18, 978); (2) from carbanile with alcohols and phenols (B. 3, 654); (3) from urea chlorides and alcohols (B. 24, 2108); and (4) from benzoylazide and alcohols (compare 1, 163, and B. 29, R. 181). The methyl ester, C₈H₅. NH. CO₂CH₃, melts at 47°, and is converted into amidosulphobenzoic ester when dissolved in sulphuric acid (B. 18, 980). The ethyl ester melts at 52°.

Urea Chlorides are produced by the action of secondary aromatic bases upon phosgene in benzene solution (B. 23, 424). Phenyl urea chloride and bromide, C6H5. NH. -

COBr, melt at 67°; compare B. 28, R. 777.

Methyl Phenyl Urea Chloride, (CH₈). (C₆H₅)N. COCl, melts at 88° and boils at 280°. Diphenyl Urea Chloride, (CaH3)2N. COCI, melts at 85°. When these urea chlorides act upon benzene in the presence of AlCl₃ they form the amides of benzoic acid (synthesis of aromatic acids, B. 20, 2118; 24, 2108).

A tetrasubstituted oxamide (B. 25, 1819, 1825) is produced when sodium in ethereal

solution acts upon di-p-tolyl-urea chloride, melting at 102°.

Phenylated Ureas.—Phenyl urea, CO<NH. CoHs, is prepared by evaporating the aqueous solution of aniline hydrochloride and potassium isocyanide (B. 9, 820), and by the action of ammonia upon carbanile. It melts at 144°.

sym.-Alkylphenyl Ureas are produced in the action of aniline upon isocyanic esters, or of phenyl isocyanide (p. 89) upon alkylamines. sym. Ethylphenyl Urea, C₂H₅NII-

CONHC₆H₅, melts at 99°.

unsym. Alkylphenyl Ureas are obtained from alkyl aniline hydrochloride and potassium isocyanide. unsym. - Ethylphenyl Urea melts at 62°.

sym. Diphenyl urea, CO < NH . C₆H₅, carbanilide, melting at 235° and boiling at NH . C₆H₅, carbanilide, melting at 235° and boiling at 260°, is formed (1) by the action of phosgene gas on aniline (B. 16, 2301); (2) by the union of carbanile with aniline (A. 74, 15); (3) by the action of mercuric oxide or alcoholic potash upon s.-diphenyl thiourea (A. 70, 148), and (4) by heating aniline with urea to 170°. It is most readily obtained (5) by heating monophenyl urea with aniline to 190° (B. 9, 820), or (6) by heating diphenyl carbonate with aniline to 170° (B. 18, 516).

Carbanilide consists of silky needles, easily soluble in alcohol and ether, but sparingly soluble in water. Diphenyl urea chloride, heated to 100° with alcoholic ammonia, yields unsymmetrical diphenyl urea, $CO < N(C_6H_5)_2$, melting at 189°, and when dis-N(C₅H₅)₂, melt-Triphenyl urea, CO < NHC₆H₅ tilled yielding diphenylamine and cyanic acid. ing at 136°, and tetraphenyl urea, $CO < \frac{N(C_6H_5)_2}{N(C_6H_5)_2}$, melting at 183°, have also been

obtained from diphenyl urea chloride (B. 9, 398).

Cyclic Alkylenphenyl Urea Derivatives (compare vol. 1, Derivatives of Urea): Ethylene Phenyl Urea, see B. 24, 2192. Trimethylene Phenyl Urea (B. 23, 1173).

Ethylene Carbanilide, CO

N(C₆H₅). CH₂, melts at 183° (B. 20, 784). Trimethylene Carbanilide melts at 153° (B. 20, 783).

Ureides of the Phenylated Ureas of monocarboxylic acids.

Acetyl Phenyl Urea, CH₂CO. NH. CO. NH. C₂H₃, melts at 183°. Acetyl Carbanilia,

C₄H₅. NH. CO. N(CO. CH₂)C₄H₅, melts at 115° (B. 17, 2882).

Ureides of Oxy-acids, Glycolyl-phenylurea, phenyl-hydantoin, is obtained on heating phenylglycin to 160° with urea. It melts at 160°.

Diphenyl Hydantoin melts at 139° (B. 25, 2274).
Phenylated Pseudourea Derivatives.—Ethyl Isodiphenyl Urea, Anilido-phenylcarbamic Ethyl Ether, C6H5N: C(O. C2H5)NH. C6H5, is an oil. It results on heating carbodiphenylimide with alcohol to 160-190°, or, better, with sodium alcoholate (B. 27, 926; 28, 573).

Phenylated Ureides of Carbonic Acid.—Phenylallophanic Ester, C₂H₅NH... CO. NH. CO₂C₂H₅, melts at 120° (J. pr. Ch. [2] 32, 18). Diphenylallophanic Acid, see B. 4, 246. Diphenylbiuret, C₂H₅NH. CO. NH. CO. NH. C₂H₄, melts at 210° (B. 4, 255). Triphenylbiuret melts at 147° (B. 4, 250). Phenylhydroxyl Urea, C, H, NH. CO. NH. OH, melts with decomposition at 140°, and results from the

action of hydroxylamine hydrochloride upon carbanile (A. 263, 264).

Phenylsemicarbazide, Phenylcarbanic Hydraside, CallyNH.CO.NH.NH, melting at 120°, is isomeric with the phenylsemicarbazide or carbamic phenylhydrazide (see this), obtained from phenylhydrazine salts and potassium cyanate. It is also produced by carefully decomposing its acetyl derivative with acids. This is formed upon boiling benzazide with acethydrazide in acetone solution; nitrogen is evolved at the same time (B. 29, R. 982):

$$C_aH_5CON_2 + NH_2 \cdot NH \cdot CO \cdot CH_2 = C_aH_5NH \cdot CO \cdot NHNH \cdot CO \cdot CH_2 + N_2$$

Phenylated Derivatives of the Thiocarbamic Acids and of Thiourea.—Phenylcarbamic Thiomethyl Ester, C_6H_5 . NH. CO. SCH₃, melting at 83°, and the

ethyl ester, melting at 74°, are formed when diphenylamidine thioalkylens are heated with dilute sulphuric acid to 180° (B. 15, 339).

Phenyl Sulphurethane, Xanthogen Anilide, Thiocarbanilic Ethyl Ester, C₆H₆. NHCS. OC₂H₅, or C₆H₆N: C(SH)OC₂H₃, melting at 71°, is produced when alcohol at 120°, or alcoholic potash, acts upon phenyl mustard oil. It is rearranged by primary and secondary bases into phenyl sulpho-ureas. It breaks down upon distillation into phenyl mustard oil and alcohol (B. 15, 1307, 2164). Alkaline potassium ferricyanide oxidizes it

to ethoxy-mustard oil, or ethoxybenzothiazole, $C_8H_4 < \sum_{S}^{N} > C.O.C_2H_8$ (see this). Like the phenylthioureas (see below), it dissolves in the alkalies, and forms metallic compounds with silver, mercury, and lead.

Phenylimidothiocarbonic Acid, $C_6H_5N:C<_{SH}^{OH}$, is not known.

When alkyl iodides act upon the metallic compounds of the phenylsulphurethanes or the free phenylsulphurethanes, we obtain the alkyl derivatives of phenylimidothiocarbonic acid (see above). The reaction is very probably analogous to that occurring with the thioacetanilides (p. 83) and the phenyl sulphoureas. The oxyethy lihio-methyl ester, C₆H₅. N:C<\(\frac{OC_2H_5}{SCH_3}\), boils with partialde composition at 260°. The di-ethyl compound melts at 30° (A. 207, 148).

Phenyl Dithiocarbamic Acid Derivatives .- When the acid is liberated from its salts it decomposes into aniline and CS₂. Its potassium salt, C₆H₅NHCSSK, is formed when potassium xanthate is boiled with aniline. It consists of golden-yellow needles (B. 24, 3022). The methyl ester melts at 87-88°; the ethyl (Phenyl dithio-urethane)

àt 60°. They are produced by warming phenyl mustard oil with mercaptans.

When these dithio urethanes are heated, they decompose into their generators. They dissolve in alkalies.

Ethyl Phenyldithiourethane, $CS < {S \choose S}, {C_2 \choose B_5}, {C_6 \choose B_5}$, melts at 68° and boils at 310°. It is formed by heating alkylized ethyl diphenyl-amidine thioethyl (p. 87) to 160° with CS₂. These compounds are very stable, no longer soluble in alkalies, and are not desulphurized by mercuric oxide or an alkaline lead solution. They form so-called addition products (B. 15, 568, 1308) with methyl iodide. Phenyl sulphurethane and diphenyl-thio-urea do the same.

Phenyl thiuramsulphide, S(CSNHC₆H₅)₂, melts at 137° (B. 24, 3023).

Methyl phenyl thiocarbamin chloride, (CH₃)C₅H₅N. CSCl, melting at 35°, is obtained from methyl aniline and thiophosgene (B. 20, 1631).

Phenyl sulphoureas (compare vol. I: sulphoureas).

Phenylthiurea, CS<NH. C₆H₆, Sulphocarbanilamide, melting at 154°, is formed

by the union of phenyl-mustard oil with ammonia.

S is replaced by O and phenylurea formed on boiling with silver nitrate. Mercuric

oxide converts it into phenylcyanamide. (For the action of methyl iodide see B. 25, 48.) s-Diphenyl-thiurea, CS NH. C₆H₅, Sulphocarbanilide, consists of colorless, shining leaslets, melting at 151° (B. 19, 1821), and readily soluble in alcohol. It is produced (1) by the union of phenyl-mustard oil with aniline in an alcoholic solution; (2) by boiling aniline with CS, and alcoholic potash with the removal of hydrogen sulphide.

Numerous reactions of sulphocarbanilide are known: (1) Iodine converts it into sulphocarbanile and a-triphenyl-guanidine. (2) When boiled with concentrated hydrochloric acid it decomposes into phenyl-mustard oil and aniline; the mixed symmetrical thiureas, $C_8H_6NH \cdot CS \cdot NH \cdot C_2H_5$, undergo, under like treatment, a decomposition into two mustard oils and two anilines (B. 16, 2016). (3) S is replaced by O, and the product is sym. diphenylurea, if diphenylthiurea be boiled with mercuric oxide (p. 85). (4) In a benzene solution mercuric oxide produces carbodiphenylimide (p. 90). (5) In the action of ammonia and lead oxide diphenyl guanidine is produced, while with aniline triphenyl-guanidine is formed.

Phenyl- and sym.-diphenyl-thiureas are soluble in alkalies, forming salts in which the

metal is combined with sulphur (as in the case of thioacetanilide, p. 83).

See B. 17, 2088; 23, 815; 26, 1686, upon the alkyl phenyl thiureas.

unsym.-Diphenylthiurea, melting at 198°, has been prepared from diphenylaminesulphocyanide (B. 26, R. 607).

Triphenylthiurea melts at 152° (B. 17, 2092). Tetraphenylthiurea, $CS < \frac{N(C_0H_5)_2}{N(C_0H_5)_2}$, is obtained by heating triphenylguanidine (p. 88) with carbon disulphide. It melts at 195° (B. 15, 1530).

Phenylthio-hydantoins.—Although the product formerly regarded as thio- or sulphhydantoin has proved to be pseudothiohydantoin (compare vol. 1), there are still aromatic phenylsulphydantoins known.

C₆H₅—N—CO CS NH.CH.CH₃ or HS.C N—CH.CH₃, Phenyl-a-methylsulphydantoin, melting at 184°, is produced on melting together phenyl-mustard oil and alanine (B. 24,

Phenylated Pseudosulphourea Derivatives.—Such compounds are obtained, for example, from phenyl and sym. diphenyl thiourea by the action of alkyl iodides and caustic alkali, or, better, upon digesting them with alkyl iodides or bromides in alcoholic solution (B. 25, 48). In the second case the iodohydrate of a base is produced. The latter is liberated on treating the former with a sodium carbonate solution, and is capable of taking up additional alkylogen. When digested with alcoholic potash, the imidophenylcarbamic thio-esters split off mercaptans.

Imidophenylcarbamic-thiomethyl Ester, $C_8H_8NH>CS$. CH_8 , melts at 71°.

Diphenylamidine-Thiomethyl, Phenylimidophenylcarbamic-thiomethyl Ester, C_8H_5 ...

NH C. S. CH₃, melts at 110°, from which would follow that the methyl-group is attached to sulphur. Both these compounds, when heated with dilute sulphuric acid, decompose into thiomethyl phenylcarbaminate.

When heated to 120° with alcoholic ammonia, phenyl-guanidine and mercaptan are

obtained.

If heated with carbon disulphide, the products are phenyl-mustard oil, and phenyl-

dithiocarbamic esters (B. 15, 343).

With CH₂I₂, CH₃Br, CH₃Br, CH₂Br, CH₂Br, diphenylthiourea affords cyclic derivatives of pseudothiourea (B. 21, 1872):

The ethylene derivative contains the so-called thiazole ring, while the trimethylene compound contains the pentathiazole ring-the next higher ring, homologous with the thiazole ring.

Pseudo-phenylthiohydantoic acid, $HN: C < NH \cdot C_0H_5$ and Pseudo-diphenylthiohydantoic acid, C_0H_5 $N: C < NH \cdot C_0H_5$ are obtained from phenyl- and diphenylthiourea by the action of chloracetic acid. By the elimination of water both of these compounds pass into psuedo-phenylthiohydantoin, HN: $C < S = CH_2$, melting at 178°, and pseudo-diphenylthiohydantoin, $C_8H_8N:-C < S = CH_2$, melting at 176°. Boiling dilute hydrochloric acid converts both com-

pounds, by water absorption, into phenyl-mustard oil acetic acid, OC < N(C₈H₆) CO S CH₁ (A. 207, 128; B. 14, 1660); ammonia and aniline are liberated simultaneously

Phenylhydroxy-thio-urea, C₆H₅. NH. CS. NH. OH, melting at 106°, is obtained from hydroxylamine and phenyl mustard oil. It decomposes very readily into water, sulphur, and phenylcyanamide (B. 24, 378).

Phenylthiosemicarbazide, C₆H₅NH.CS.NH.NH₂, melts with decomposition at 140°. It is formed from phenyl mustard oil and hydrazine hydrate. It is rearranged by aldehydes with the production of hydrazones. Its acidyl derivatives readily part with water and form thiobiazolines (see these). The benzoyl derivative manifests a peculiar behavior in that when it is treated with acetyl chloride it parts with water and a phenylimido-phenylthiobiazoline results; with benzoyl chloride, however, a diphenyl triazole mercaptan (see triazoles) is produced (B. 29, 2914):

Phenylated Guanidine Derivatives (see vol. I, Guanidines).

Diphenyl-guanidine, HN: $C < NH \cdot C_0^e H_6$ (Melaniline), melting at 147°, is produced by the action of cyanogen chloride upon dry aniline, and by digesting cyananilide (p. 90) with aniline hydrochloride. It is, like guanidine, a mono-acid base. Carbon disulphide transforms it into sulpho-carbanilide and sulphocyanic acid.

a-Triphenyl-guanidine, C_6H_5 , $N:C<\frac{NH\cdot C_6H_5}{NH\cdot C_6H_5}$, melting at 143°, is obtained on heating diphenyl-urea or diphenyl-thiurea, alone or with reduced copper, to 140°. It is most readily prepared by digesting an alcoholic solution of diphenyl-thiurea and aniline, with litharge or mercuric oxide (or by boiling with an iodine solution). Heated with CS, it reverts again to diphenyl-thiurea and phenyl mustard oil.

 β -Triphenyl-guanidine, C=NH β -Triphenyl-guanidine, C=NiH, melting at 131°, is obtained by heating NH. C₈H₅ cyananilide with HCl-diphenylamine. It decomposes into diphenylamine, phenyl mustard oil, and sulphocyanic acid when heated with carbon disulphide.

sym.-Tetraphenyl-guanidine, NH: $C < N(C_6H_5)_2$, melting at 130°, is produced by the action of CNCl upon diphenylamine at 170°

Phenylated Nitriles and Imides of Carbonic Acid (compare vol. 1).

Phenyl Isocyanate, Carbanile, CO: N. C₆H₅, is a mobile liquid, boiling at 163°, and has a pungent odor, provoking tears. It is produced in the distillation of oxanilide, or, better, carbanilic esters with P2O5 (B. 25, 2578 Anm.), also from diazobenzene salts, by the action of potassium cyanate and copper (B. 25, 1086). It may be most readily obtained by leading COCl, into fused aniline hydrochloride (B. 17, 1284), or by heating phenyl mustard oil to 170° with HgO (B. 23, 1536). Carbanile is perfectly analogous to the isocyanic esters in chemical deportment. It yields diphenylurea with water. It combines with alcohols and phenols to form carbanilic esters; this is a reaction which may be employed in determining alcoholic hydroxyls (B. 18, 2428; 2606). It reacts similarly with the SH-group, as well as with the hydroxyl groups of the aldoximes and ketoximes. It does not react with the groups C: O and C: S (B. 25, 2578). With ammonia carbanilamide, CO<NH. C₆H₅, is formed.

Diazo-amido-compounds—e. g., C₈H₅. N₂. NHR—react with phenylisocyanate.

so doing the hydrogen of the amido-group is replaced (B. 22, 3109).

The preceding reactions, occurring in the absence of water (thus avoiding electrolytic dissociation), proceed in the normal way. Rearrangements do not take place, hence they are well adapted for the determination of constitution (Goldschmidt, B. 23, 2179). On heating phenylisocyanate with benzene and AlCl₃, we get benzoylanilides (see syn-

theses of benzoic acid and its homologues).

Triphenylisocyanurate, $(CON)_5(C_6H_5)_3$, melting at 275°, is produced (1) by the polymerization of phenylisocyanate upon heating it with potassium acetate (B. 18, 3225); (2) by heating triphenylisomelamine (p. 90) with concentrated hydrochloric acid to 150° C. Its isomeride is

Triphenylcyanurate, C₃N₃(O. C₆H₅)₃. This is produced by the action of cyanogen

chloride or cyanuric chloride upon sodium phenate. It melts at 224°.

Isocyanphenyl Chloride, Phenylimidocarbonyl Chloride, C₆H₅N: CCl₂, boiling at 200° (corr.), is a colorless oil with a penetrating odor. It is produced when chlorine acts upon phenylisocyanide in chloroform solution, and also from phenyl mustard oil and chlorine (B. 26, 2870). Aniline changes it to a-triphenyl guanidine (A. 270, 282).

Phenyl-sulphocyanate, C₆H₅. S. CN, boiling at 131°, is isomeric with phenyl mustard oil, and with Methenyl-amido Thiophenyl, Coll (see amido thiophenyl, Coll (see It is formed (1) when hydrosulphocyanic acid acts upon diazobenzene sulphate (see this), and (2) cyanogen chloride upon the lead salt of thiophenol. In its reactions it is analogous to the sulphocyanic esters.

Phenyl Mustard Oil, Sulpho-carbanile, Phenyl-isothiocyanic Ester, CS: N. C. H., is a colorless liquid, with an odor resembling that of mustard oil, and boils at 222°. It is obtained by boiling diphenyl thio-urea with sulphuric or concentrated hydrochloric acid, or, what would be best, with a concentrated phosphoric acid solution (B. 15, 986), and by the action of an alcoholic iodine solution (with triphenyl guanidine), or CSCl₂, upon aniline. It is converted into benzonitrile when heated with reduced copper or zincdust.

On this reaction is founded a procedure to replace the group NH, by COOH—that is, to convert the anilines successively into thio-ureas, mustard oils, nitriles, and acids. (See synthetic methods of producing the benzoic acids and their homologues.)

If heated with anhydrous alcohols to 120°, or by the action of alcoholic potash, it is

converted into phenyl-thio-urethanes (p. 86).

It forms phenyl-thio-ureas with ammonia, the amines, aniline hydrazine, and hydroxylamine. Chlorine converts it into isocyanphenylchloride (see above).

Phenyl mustard oil, under the influence of aluminium chloride, combines with aromatic 11-8

hydrocarbons, phenol ethers, and thiophenol ethers, to produce the thioanilides of carboxylic acids (B. 27, 1733).

Phenylated Cyanamide Derivatives (compare cyanamide, vol. 1).

Phenyl Cyanamide, Cyananilide, C_8N_5 . NH. $CN + \frac{1}{2}H_2O$, melts at 47°. When allowed to stand in a desiccator it loses water, becomes liquid, and in moist air reverts to the hydrate. On long standing or when heated it polymerizes to *Triphenyl-isomela-*mine. It is formed on conducting CNCl into a cooled ethereal solution of aniline, and by digesting phenyl-thiurea with litharge, or by heating it with lead acetate and alkali (B. 18, 3220). It is readily soluble in alcohol and ether. It forms phenyl-thiurea with H₂S.

Diphenylcyanamide, (C₆H₅)₂N. CN, melting at 73°, is formed when an ammoniacal

silver solution (B. 26, R. 607) acts upon unsym.-diphenyl thio-urea (p. 87).

Carbodiphenylimide, CaHaN: C: NCaHa, is a thick liquid, which suffers decomposition when distilled at the ordinary pressure, but unaltered at 218° under 30 mm. pressure. Distilled at the ordinary pressure it polymerizes in part to a modification melting at 161°; this has the trebled molecular formula (B. 28, 1004; compare B. 29, 270).

Carbodiphenylimide is produced by the action of mercuric oxide upon sym.-diphenylthiurea in benzene solution, or by the distillation of a-triphenyl-guanidine. absorbs water it yields sym.-diphenyl urea. It combines with H₂S to sym.-diphenyl thiurea, and with aniline to a-triphenyl-guanidine. Compare also o-phenylenediamine.

The compounds C_6H_5N : CCl. NH. C_6H_5 and C_6H_5NH . CCl₂. NH. -C₆H₆ (B. 28, R. 778) are formed when hydrochloric acid gas is conducted into the benzene solution of carbodiphenylimide.

Triphenylmelamine, Triphenylcyanurtriamide, C3N3(NH. C6H5)2, melting at 228°, is produced in the action of cyanuric chloride on aniline, or by heating ethyl trithiocyanuric ester with aniline to 250-300° (B. 18, 3218).

Hexaphenylmelamine, C₃N₃[N(C₆H₅)₂]₃, melts at 300°, and is formed by letting

cyanuric chloride act upon diphenylamine.

Triphenylisomelamine, C₃N₃(C₆H₆)₃(NH)₃, melts at 185°. On long standing phenylcyanamide polymerizes to this compound. Or, it is produced when cyanogen bromide acts on aniline. On warming with hydrochloric acid it successively loses its NHI groups, oxygen entering, and the sole product is the triphenyl ester of isocyanuric acid (p. 89) (B. 18, 3225). In addition to the normal triphenylmelamine and triphenylisomelamine, asymmetrical triphenylamines are known (B. 18, 228).

Anilides of Dicarboxylic Acids.—Oxalic acid and its homologues, as well as the unsaturated dicarboxylic acids, form anilic acids and dianilides, corresponding to the amino acids and the diamides. Those dicarboxylic acids capable of forming anhydrides yield also anils or phenylimides, corresponding to the imides.

The anilic acids are obtained (1) by partial decomposition of the dianilides; (2) on mixing the ethereal or chloroform solutions of the anhydrides with aniline (B. 20, 3214); (3) by the breaking down of the anils. The latter are reformed from the anilides by treatment with PCl₅ (B. 21, 957), or with acetyl chloride. They also appear on heating the acids or anhydrides with aniline. A large number of these derivatives have been mentioned in the first volume in connection with their respective acids.

Phenylamine Derivatives of Oxalic Acid.—Oxanilic Acid, CeH5. NH. CO. CO₂H, melting at 150° (see A. 270, 295, for an isomeric acid melting at 210°), is formed by heating oxalic acid and aniline to 140° (B. 23, 1820), by the action of alcoholic potash upon oxanilide, and when citraconanilic acid is oxidized with potassium permanganate (B. 23, 747). Its methyl ester melts at 114° (A. 254, 10), the ethyl ester at 66°, and the chloride at 82° (B. 23, 1823).

Oxanilide, (CONHC₈H₆)₂, melts at 245°. Tetra-p-tolyloxamide, [CON[4]-(C₈H₄[1]CH₃)₂]₂, from p-ditolylurea chloride, melts at 127° (p. 85). Oxanildioxime, [C:(NOH)(NHC₈H₅)]₃, formed from dibromglyoxime peroxide, melts with decomposition at 215°. Half-ortho-oxalic-dianilido-methyl Ester, CO₂. CH₃. C(NH. C₈H₅)₂. OCH₃, and Dimethyl Phenylimido-oxalic Ester, CO₂. CH₃. C:N. C₈H₅(OCH₃), melting at 111°, are obtained from dichlor-oxalic ester and aniline (B. 28, 60).

Phenyloxamic-diphenyl-amidine, C_6H_5NHCO . C_6N_1 . C_6H_5 , melting at 134°, is prepared from half-ortho-oxalic ester and oxanildichloride acid ethyl ester (A. 184, 268).

o-Nitro-oxanilic Acid melts at 112°. o-Dinitro-oxanilide (A.

209, 369).

í

Malonanilic Acid, CH₂ < CO. NH. C₆H₅, melts at 132° and decomposes into CO₂ and acetanilide. It is produced by a peculiar transposition of acetylphenyl carbaminate of sodium when heated to 140° (B. 18, 1359). PCl₅ converts it into trichlorquinoline (B. 18, 2975).

Malonanilide, CH₂(CONHC₆H₅)₂, melts at 223° (B. 17, 135, 235).

Succinanilic Acid and Succinanil (see vol. I, Succinimide).

For fumaranilic acid, fumaranilic chloride, fumardianilide, maleInanilic acid, maleinanil, dichlormaleinanil, dichlormaleinanil dichloride, dimethyl dichlormaleïnanilic ester, dichlormaleïnimide anil, dichlormaleïndianil, citraconanilic acid, citraconanil, itaconanilic acid, consult the corresponding acids described in vol. I.

Anilido-dicarboxylic Acids.—Compare phenylasparagine anilic acid, phenylasparagin anil; for β -anilidopyrotartaric acid and pseudoitaconamilic acid, see amidosuccinic acids, vol. I.

Phenylated Ureides of Dicarboxylic Acids.—Phenylparabanic Acid,

 $N(C_6H_5)$ —CO _CO, melting at 208°, and Diphenylparabanic Acid, melting at 204°, CO<NHare formed, for example, by the action of ethoxalic chloride upon the corresponding carbamides (J. pr. Ch. [2] 32, 20).

Aniline Substitution Products.—It is only the aniline derivatives, among the substitution products of the primary phenylmines, which deserve particular consideration, for it was with them that the regularities of substitution obtaining among the aromatic amido-bodies were observed, and they were the intermediate stages in numerous instances where constitution was to be determined.

Aniline Haloids.—Formation.—(1) Aniline, like phenol, is more readily substituted than benzene. When chlorine or bromine acts upon the aqueous solutions of aniline salts, the halogen atoms enter the [2,4,6] position. Starting with acetanilide (p. 82) chlorine and bromine produce first p- and o monosubstitution products; these are immediately converted into o-p-disubstitution derivatives. If, however, chlorine or bromine be allowed to act upon aniline, in the presence of concentrated sulphuric or hydrochloric acid, m-compounds will be produced. The fact that the amido-group combines with strong acids demonstrates its negative character (B. 22, 2903). The anilines substituted in the meta-position yield tetra- and penta-substitution products (B. 15, 1328).

Indicate can substitute the anilines directly; the resulting hydriodic acid combines with the excess of base: $2C_8H_5NH_2 + I_2 = C_6H_4I.NH_2 + C_6H_5NH_2$. HI.

2. The nonohalogen anilines can be readily obtained from the monohalogen nitro-

benzenes, which in turn are derived from the nitro-amido-derivatives. The change is effected through the diazo-bodies (p. 99)-e.g.:

$$C_{e}H_{4} <_{NH_{2}}^{NO_{2}} \xrightarrow{\hspace*{1cm}} C_{e}H_{4} <_{Br}^{NO_{2}} \xrightarrow{\hspace*{1cm}} C_{e}H_{4} <_{Br}^{NH_{2}}.$$

p-Chloraniline is a stronger base than the o- and m-bodies (B. 10, 974). It has also been obtained by the electrolytic reduction of nitrobenzene in concentrated hydrochloric acid solution. It is very probable that C₈H₅. NHCl is formed at first, but subsequently rearranges itself into p-chloraniline (p. 65 and B. 29, 1895).

	[1,2]-, 0-		[1,3]-, m-		[1,4]-, p-		
	M. P.	B. P.	M. P.	B. P.	M. P.	B. P.	
FIC ₆ H ₄ NH ₂ , CIC ₆ H ₄ NH ₂ , BrC ₆ H ₄ NH ₂ ,	liquid	 207° 229°	liquid 18°	 230° 251°	liquid 70° 63°	188° 230° decom-	(A. 243, 222) (A. 176, 27) (B. 8, 364)
IC ₆ H ₄ NH ₂ ,	56°	_	27°		63°	poses —	(G. 17, 487)

Mention may be made of the following higher aniline substitution products. lide yields:

a-[1NH₃,2,4] Dichloraniline, melting at 63° and boiling at 245° (B. 7, 1602). a-[1NH₄,2,4] Dibromaniline, melting at 79° (A. 121, 266). β -[1,4,2NH₄] Dichloraniline, melting at 54° and boiling at 250° (A. 196, 215) and β -[1,4,2NH₂] Dibromaniline, melting at 51° (A. 165, 180), have been obtained from the corresponding nitro-compounds.

Aniline, acted upon by chlorine and bromine, yields:

[1NH2,2,4,6] Trichloraniline, melting at 77° and boiling at 262° (J. pr. Ch. [2] 16, 449; B. 27, 3151).

[1NH₂, 2, 4, 6]-Tribromaniline, melting at 119° (B. 16, 635). The five benzene hydrogen atoms in aniline can be substituted by chlorine or bromine :

Pentachloraniline melts at 232°. Pentabromaniline melts at 222°. Halogen benzenes are produced by eliminating the amido-group by means of the diazo-compounds (see these).

Nitranilines, NO₂C₆H₄NH₂, are isomeric with diazobenzene acid, C₆H₅NHNO₂

(p. 99). Nitric acid attacks aniline energetically, and resinifies it with ease.

(1) In order to get mono- and disubstitution products acetanilide is nitrated (p. 82). The amido-group is protected by the acetyl group; the immediate products are p- and o-nitracetanilide. When sniline is nitrated in the presence of concentrated sulphuric acid and in the cold, not only p- and o-bodies result, but also metanitraniline (B. 10, 1716; 17, 261). The quantity of the latter is greater the more sulphuric acid there is present ·261). (p. 91).
The union of the amid-group and the transposition into an acid group occur simul-

taneously, giving rise to a meta-substitution product (p. 69).

The three isomerides are separated by means of their varying basicity. When their acid solution is neutralized, the m-body is first precipitated, then follow the p- and the o-nitranilines (B. 28, 1954).

(2) The nitranilines can be prepared by heating haloid nitrobenzenes to 150-180° with alcoholic ammonia; or by heating the ethers of the nitrophenols—e.g., C.H. (NO2). O. C₂H₅, with aqueous ammonia. In both instances the para- and ortho-compounds, and not the meta-, react.

(3) By the partial reduction of polynitro-derivatives (p. 70).

(4) Upon heating nitroamido benzene sulphonic acids with hydrochloric acid to 170° (B. 18, 294).

(5) o- and p-Nitranilines are formed in the rearrangement of diazobenzene acid (p. 99):

The nitro-anilines link the diamido- and dinitro-benzenes to the nitro-haloid-, amidohaloid-, and dihaloid benzenes:

$${}^{C_{6}H_{4}} < \stackrel{NH_{2}}{NH_{2}} \leftarrow {}^{C_{6}H_{4}} < \stackrel{NO_{2}}{NO_{2}} \rightarrow {}^{C_{6}H_{4}} < \stackrel{NO_{2}}{NH_{2}} \rightarrow {}^{C_{6}H_{4}} < \stackrel{NO_{2}}{Br} \rightarrow {}^{C_{6}H_{4}} < \stackrel{NH_{2}}{Br} \rightarrow {}^{C_{6}H_{4}} < \stackrel{Br}{Br}$$

When ortho- and para-nitranilines (not meta) are boiled with alkalies, they part with N113, and are converted into their corresponding nitrophenols, CaH4(NO2). OH; the diand tri-nitranilines react even more readily.

The nitranilines approach in character the acid amides as the number of nitro-groups in them increases.

Ammonia converts the corresponding dinitrophenols or polynitrohaloid benzenes into:

a-[1NH₄,2,4]-Dinitraniline, melting at 182°.
$$\beta$$
-[1NH₂,2,6]-Dinitraniline, melting at 138°.

[1NH₂,2,4,6]-Trinitraniline, C₆H₂(NO₂)₃. NH₂, *Picramide*, is obtained from picric acid through its ether, or by means of picryl chloride (p. 68). The latter reacts with ammonia, even in the cold. It forms orange-red needles, and melts at 186°. It forms picric acid when heated with alkalies:

$$C_6H_2(NO_2)_3$$
. $NH_2 + KOH = C_6H_2(NO_2)_3$. $OK + NH_3$.

sym.-Trinitroxylidine, melting at 206°, is obtained from trinitrochlorxylene and ammonia (B. 28, 2047).

Nitrodiphenylamines.—Chlor- and brom-benzene do not react with aniline, but o-bromnitrobenzene and polynitrohaloid benzenes are changed by it into nitrodiphenylamine (together with an aniline halogen hydride). It is also possible to introduce an acid radical—e. g., benzoyl—into the imido-group, and then nitrate. Hexanitrodiphenylamine is produced in the direct nitration of diphenylamine.

o-Nitrodiphenylamine melts at 75° (B. 22, 903). p-Nitrodiphenylamine melts at 132° (B. 15, 826). p-Dinitrodiphenylamine melts at 214° (B. 15, 826).

[2,4,6]-Trinitrophenyl-phenylamine, from picryl chloride, melts at 175° (B. 3, 126). Trinitroxyl-phenylamine melts at 175° (B. 28, 2047). Hexanitro-diphenylamine is an acid, melting at 238°. It dissolves with a purple-

red color, in the alkalies, forming salts. Its ammonium salt occurs in commerce as a brickred powder. It was employed under the name Aurantia before the introduction of the azo-dyes, to color wool and silk a beautiful orange.

NITROSO-DERIVATIVES OF THE PRIMARY, SECONDARY AND TERTIARY AROMATIC AMINES.

Formation.—(1) When the nitrosamines of monomethylaniline or diphenylamine (p. 97) are treated with alcoholic hydrochloric acid, they rearrange themselves into p-nitroso-compounds (B. 19, 2991). (2) The p-nitroso-bodies are also produced when nitrous acid acts upon the tertiary dialkylanilines, or sodium nitrite upon their hydrochlorides (Baeyer and Caro, B. 7, 963). (3) When the nitroso-phenols are fused with ammonium acetate and ammonium chloride, they yield p-nitroso-anilines (B. 21, 729). Deportment.—When the p-nitroso-derivatives of the secondary and tertiary aromatic

amines are heated with caustic soda, they break down into sodium nitrosophenate and alkylamines (1, 163). Most chemists consider the nitroso-phenols to be the monoximes of the paraquinones. And in connection with this mode of formulation of the nitrosophenols many are also disposed to view the p-nitroso-derivatives of the secondary and tertiary aromatic amines as quinone derivatives:

$$\begin{array}{cccc} C_{0}H_{4}\left\{ \begin{bmatrix} \mathbf{I} \end{bmatrix} : O \\ \mathbf{I}_{0} & C_{0}H_{4}\left\{ \begin{bmatrix} \mathbf{I} \end{bmatrix} : N. \text{ OH} \\ \mathbf{I}_{0} \end{bmatrix} : O \\ \text{p-Quinoxime} \\ \text{p-Nitrosophenol} \end{array} \right. \\ \begin{array}{c} C_{0}H_{4}\left\{ \begin{bmatrix} \mathbf{I} \end{bmatrix} : N(CH_{0})_{2} \\ \mathbf{I}_{0} \end{bmatrix} : N(CH_{0})_{2} \\ \text{p-Nitroso-dimethyl-aniline} \end{array}$$

p-Nitroso-aniline, NO[4]C₆H₄[1]NH₂, melting at 174°, crystallizes in steel-blue needles (B. 21, 720; 28, R. 735).

needles (B. 21, 729; 28, R. 735).
p-Nitrosomethylamine, NO[4]C₄H₄[1]NHCH₅. The free base forms crystals with metallic lustre and melts at 118° C. It is soluble in dilute sodium hydroxide, and is again liberated from its solution by carbon dioxide.

When heated with sodium hydroxide, p-nitrosomethyl aniline is decomposed into

sodium nitrosophenate and methylaniline.

p-Nitroso-mono-ethyl-aniline melts at 78°.

p-Nitroso-dimethyl-aniline, NO[4]C₆II₄[1]N(CH₃)₃, melting at 85°, consists of large, green leaflets. Potassium permanganate and ferrocyanide of potassium oxidize it to p-nitrodimethylaniline. Upon reduction it yields p-amidodimethylaniline, which is so important in the dye manufacture. Sodium hydroxide resolves it into nitroso-phenol and dimethyl aniline. Its hydrochloride dissolves with difficulty in cold water. p-Nitroso-diethyl-aniline melts at 84°.

p-Nitroso-diphenylamine, melting at 143°, consists of green plates, and is produced when hydrochloric acid gas acts upon diphenylnitrosamine (B. 20, 1252; 21,

R. 227).

C. DIAMINES.

Formation.—The aromatic diamines, whose amido-groups are attached to the benzene nucleus, are formed (1) by the reduction of the three dinitrobenzenes or nitroanilines with tin and hydrochloric acid; (2) the monamines can be converted into the diamines by first changing them to amido-azo-compounds, and then decomposing the latter by reduction:

$$C_6 II_5 N = N[4]C_6 II_4[1]NII_2 + 4II = C_6 II_5 NII_2 + NII_2[4]C_6 II_4[1]NII_2$$

- (3) they can be obtained, also, from the diamidobenzoic acids by the loss of carbon dioxide when they are treated with baryta. This reaction has become of particular importance in ascertaining the constitution of the three phenylenediamines.
- (4) Diphenylated diamidobenzenes, $C_6H_4(NH\cdot C_6H_5)_2$, are produced when dioxybenzenes—e. g., resorcinol and hydroquinone (see these)—are treated with aniline and CaCl₂ or ZnCl₂.

Properties.—The diamines are colorless solids volatilizing without decomposition, but on exposure to the air they become colored. They are di-acid bases, forming well-defined salts. Ferric chloride imparts an intense red color to their solution. The amide hydrogen atoms can be replaced in the same manner as in the monamines.

Diamidobenzenes, or phenylenediamines, $C_eH_4(NH_2)_2$. The o-body is derived from o-nitraniline by reduction with caustic soda and zinc-dust (B. 28, 2947). The m-derivative is most easily accessible through m-dinitrobenzene (p. 67). The p-compound is obtained by the decomposition of amido-azo-benzene (Z. f. Ch. (1866) 136).

DIAMINES.

95

o Phenylenediamine is colored red, in hydrochloric acid solution, by ferric chloride, with the production of diamidophenazine hydrochloride (B. 27, 2782). In the table, see below, showing the numerous o-condensations of which the o-diamines are capable, it is o-phenylenediamine which appears most frequently as the example. o-Amidophenylurethane melts at 86°.

m-Phenylenediamine is converted by nitrous acid into triamido azobenzene (see this), or Bismarck brown. Hence, it imparts an intense yellow color to a dilute solution of nitrous acid, and can therefore be employed for the quantitative estimation of the latter in water (B. 14, 1015). Consult B. 7, 1263; 21, R. 521; 24, 2113, for the action of COCl₂, CS₂, and oxalic ester.

p. Phenylenediamine is oxidized by the oxygen of the air to dark garnet-red crystals

of Tetra-amidodiphenyl-p-azophenylene, C_6H_4 [1]N[1] C_6H_3 [2,5](NH₂), melting with decomposition at 230-231° (B. 27, 480). Manganese dioxide and sulphuric acid convert it into quinone (see this), while bleaching lime changes it to quinonedichloride (see this). p-Amido-dimethyl aniline, NH₂[4] C_6H_4 [1]N(CH₂), melting at 41° and boiling at 257°, is prepared by the reduction of p-nitroso- or p-nitrodimethyl aniline (p. 94), and by decomposing helianthine (p. 138), or p-dimethylamido-azobenzene (B. 16, 2235). Hydrogen sulphide and ferric chloride, in acid solution, impart a dark-blue coloration to its acid solution. methylene there were this lit is, therefore, a delicate coloration to its acid solution: methylene blue (see this). It is, therefore, a delicate reagent for the detection of hydrogen sulphide. Formyl-p-amido-dimethyl aniline, see B. 27, 602. Nitro-p-phenylenediamine, melting at 135°, consists of green, vitreous needles, and is obtained from [1,2,4] dinitraniline (B. 28, 1707; 29, 2284).

Diamidotoluenes, Toluylene Diamines.—The six bodies possible theoretically

are known:

 I. [ICH₃, 2,3]-Toluylene diamine melts at 61° and boils at 255° (A. 228, 243).
 ICH₃, 3,4]-Toluylene diamine melts at 88° and boils at 265°.
 [ICH₃, 2,4]-Toluylene diamine melts at 99° and boils at 280° (compare toluylene red).

4. [ICH₃, 2,6]-Toluylene diamine melts at 103° and boils at (B. 17, 1959).
5. [ICH₃, 3,5]-Toluylene diamine is a liquid and boils at 284° (A. 217, 200).
6. [ICH₃, 2,5]-Toluylene diamine melts at 64°; boils at 273°.

[1,3,4]-Toluylene diamine is the most easily accessible o-diamine. It is prepared from p-acet toluidine:

$$G_{6}H_{4}\left\{ \begin{bmatrix} 1\\ 4 \end{bmatrix} CH_{9} \xrightarrow{} C_{6}H_{3} \left\{ \begin{bmatrix} 1\\ 3 \end{bmatrix} NO_{2} \xrightarrow{} C_{6}H_{3} \left\{ \begin{bmatrix} 1\\ 3 \end{bmatrix} NO_{2} \xrightarrow{} C_{6}H_{3} \left\{ \begin{bmatrix} 1\\ 3 \end{bmatrix} NO_{2} \xrightarrow{} C_{6}H_{3} \left\{ \begin{bmatrix} 1\\ 3 \end{bmatrix} NH_{2} \right\} \right\} \right\} \left\{ \begin{bmatrix} 1\\ 4 \end{bmatrix} NH_{2} \xrightarrow{} C_{6}H_{3} \left\{ \begin{bmatrix} 1\\ 4 \end{bmatrix} NH_{2} \xrightarrow{} C_{6}H_{3}$$

[1,2,4]-Toluylene diamine is used as the starting-out substance in the preparation of toluylene red (see this).

Xylylene Diamines.—[1,3,2,4]-Diamido-m-xylene melts at 64° (B. 17, 2426). [1,3,4,6]-Diamido-m-xylene melts at 104°. [1,2,3,5]-,0-Diamido-m-xylene melts at 77°.

[1,2,3,5,6]-,o-Diamidopseudocumene melts at 90°. [1,4,3,5,6]-,p-Diamidopseudocumene melts at 78° (B. 24, 1647). Diamidomesitylene melts at 90° (A. 141, 134; 1**79**, 176), etc.

See p. 116 for the di- and tetra-alkylized phenylene diamines. Phenylated phenylene diamines or o- and p-amidodiphenylamine derivatives are formed in the so-called o- or p-semidine rearrangement of suitable hydrazobenzenes (p. 117).

THE CONDENSATIONS OF THE o-DIAMINES.

The o-diamines possess the power in a remarkable degree of forming condensation products. These usually consist of ring systems containing five or six atoms, and will be discussed in connection with the *heterocyclic* carbon derivatives. The m- and p diamines do not possess this power. The condensation occurs in that hydrogen atoms of both amido-groups of an o-diamine are replaced by polyvalent atomic groups. Frequently, when this occurs, the nitrogen atoms occupying the o-position unite with one

 Sulphur dioxide and selenium dioxide convert the o-diamines into piasthioles (see these) and piasselenoles (see these).

2. Nitrous acid produces asimides (see these).

3. The cyclic amidines are directly produced from the o-diamines on heating them with acids, their chlorides and anhydrides, as well as with aldehydes: anhydrobases or aldehydines (Ladenburg). These are substances nearly related to the glyoxalines (1, 322) or imidazoles, and will be treated later in connection with these. Such condensations have been observed also in the reduction of acidylated o-nitro-amido-compounds (Hobrecker).

4. Cyclic ureas and thiurea derivatives are formed from COCl, and SCCl, or CS, also by condensation with urea and thiurea, as well as with ammonium sulphocyanide (p. 97).

5. Cyclic guanidine derivatives are obtained by means of carbodiimides (p. 90) and phenyl mustard oils (p. 89).

6. A very interesting condensation of the o diamines is that with glyoxal and other a-dicarbonyl derivatives, as well as with grape-sugar, when quinoxalines result, with the

exit of water (Hinsberg) (1, 321).

Related six-membered rings are produced (7) when o-diamines condense with cyanogen. (8) By condensation with o-dioxybenzene. (9) unsym. Diamidophenasine is produced by the oxidation of o-phenylenediamine. (10) Dibenzene sulphone-derivatives of o-phenylenediamine condense with alkylen dihaloids—e. g., methylene iodide, ethylene bromide, trimethylene bromide. The products are cyclic diamines, from which the corresponding phenylene alkylen diamines are obtained by the splitting off of the benzene sulphone groups (B. 28, R. 756).

$$(1) \xrightarrow{SO_2} C_8H_4 \begin{cases} [1] N \\ [2] N \end{cases} S \text{ or } C_8H_4 \begin{cases} [1] N \\ [2] N \end{cases} S - \text{Piazthio} \end{cases}$$

$$(2) \xrightarrow{NO_2H} \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} N \text{ Azimidobenzene}$$

$$(3) \xrightarrow{H.CO_2H} \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} CII \text{ Benzimidazole, o-Phenylene formamidine}}$$

$$(3) \xrightarrow{C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases}} CII \xrightarrow{O-Phenylene formamidine} COCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] N \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2 \rightarrow C_6H_4 \begin{cases} [1] NH \\ [2] NH \end{cases} COOCl_2$$

The o-amidophenols and the o-amidothiophenols show condensations similar to those observed with the o-diamines.

DIFFERENCES BETWEEN THE o-, m-, AND p-DIAMINES.

I. The para-diamines are capable of yielding various dyestuffs. Mixed with primary amines (or phenols) and oxidized at the ordinary temperature, they are converted into indoamine and indophenol dyestuffs; at higher temperatures the so-called safranines are produced. When oxidized with ferric chloride in the presence of H₂S, the paradiamines, containing a free NH₂ group, yield sulphurized dyes of thio-diphenylamine (Lauth's Dyestuffs). Manganese dioxide and sulphuric acid oxidize the p-diamines to quinones, recognizable by their odor. Ferric chloride (B. 17, R. 431) imparts color to the diamines. See above, o-phenylendiamine.

2. The ortho-diamines, when acted upon by nitrous acid, yield asimido-compounds, e. g., Azimidobenzene. The meta-diamines, on the contrary, yield yellow-brown azodyes, of the type of phenylene brown. Test for nitrous acid, B. 11, 624, 627. In very acid solution, and when there is a constant excess of acid (nitrous), the meta-diamines form bisdiazo-derivatives. Nitrous acid (or NaNO₂) converts the para-diamines (their salts) into bisdiazo-compounds.

3. When the hydrochlorides of the three isomerides are digested with ammonium sulphocyanide, disulphocyanides, like $C_6H_4 < {}^{\rm NH_2}_{\rm NH_3}$. HSCN, are produced. On heating these to 120° we discover that the orthodiamines are changed to cyclic sulphureas, $C_6H_4 < {}^{\rm NH}_{\rm NH}>$ CS. These are not altered by digestion with an alkaline lead-solution (not desulphurized); while the derivatives, obtained from the meta- and para-diamines, are immediately blackened by the alkaline lead-solution (Reaction of Lellmann, B. 18, R. 326).

4. The diamines unite in a similar manner with the mustard oils. If these products be fused, those from the ortho-diamines decompose into cyclic phenylenesulphurea and dial-kylsulphureas; the fused mass instantly becomes crystalline. The meta-diamine derivatives melt without decomposition, while those of the para-, after fusion, are completely

broken up (B. 18, R. 327, and 19, 808).

5. The o-diamines show a series of other condensation reactions, which have been tabulated above, and as the m- and p-diamines behave differently in these transpositions, they will answer for the distinction of the o-derivatives from the other two classes. The behavior toward *phenanthraquinone* is used for the detection of the o-diamines. A more delicate test is that with *croconic acid* (B. 19, 2727). Both tests are based upon the formation of quinoxaline derivatives

Triamines.—The three triamidobenzenes possible theoretically are known, although

the symmetrical body only in the form of its salts.

The adjacent (1,2,3) is obtained from triamidobenzoic acid (from chrysanisic acid). When pure it melts at 103° and boils at 330° (A. 163, 23). The unsymmetrical (1,2,4), melting at 132° and boiling at 340°, is obtained by the decomposition of chrysoldine (B. 10, 659; 15, 2196), or diamidoazobenzene (p. 116), and from compounding nitroamido-derivatives (B. 19, 1253). When oxidized by air it changes to a eurhodine dyestuff (B. 22, 856). [1CH₃, 2,3,4]-Triamidotoluene (B. 14, 2657). a-Diamidodimethyl Aniline boils at 178° (22 mm.); see B. 29, 1053.

line boils at 178° (22 mm.); see B. 29, 1053.

Tetramines.—v-,[1,2,3,4]-Tetra-amidobenzene is obtained by the reduction of diquinoyl tetroxime (B. 22, 1649). The symmetrical (1,2,4,5) variety is formed by the reduction of dinitro-m-phenylenediamine. It exhibits all the reactions of the ortho- and

para-diamines (B. 22, 440).

Pentamines.—Penta-amidobenzene, from trinitro-m-phenylenediamine, is very

unstable on exposure to the air.

Penta-amidotoluene, CH₃. C₆(NH₂)₅, is formed from trinitro-s-toluylene diamine (B. 26, 2304).

As the number of amido-groups increases the polyamines become more unstable.

6. PHENYL-NITROSAMINES.

Nitroso-compounds are obtained when potassium nitrite acts upon the hydrochlorides of secondary aromatic bases. This procedure is similar to that employed with the aliphatic nitrosamines. It is a reaction which can be used to distinguish and separate secondary from primary and tertiary bases, as the nitrosamines are precipitated as oils from the acid solution of a mixture of bases. The phenyl-nitrosamines in alcoholic or ethereal solution, when treated with hydrochloric acid gas, pass into p-nitroso-anilines (p. 94):

They change into hydrazines upon reduction, or break down into ammonia and the original secondary bases. They are volatile with steam (B. 10, 329; 22, 1006; A. 190,

151) and decompose upon distillation.

The nitrosamines are not only intimately related to the secondary amines and hydrazines, but also to the diazo-compounds. Diazobenzene potassium may be readily rearranged into isodiazobenzene potassium, which yields phenylmethyl-nitrosamine with methyl iodide. unsym.-Phenylmethyl-hydrazine results from the reduction of phenylmethylnitrosamine. Potassium diazobenzolate is formed by the oxidation of isodiazobenzene potassium. The latter and methyl iodide combine to methyl a-diazobenzolate, the phenylmethyl-nitramine, which can be reduced to phenylmethyl-nitrosamine and unsym. These relations are indicated in the following diagram: phenylmethyl-hydrazine.

$$\begin{array}{c} C_{g}H_{5}N_{2}.OK \longrightarrow \begin{array}{c} Isodiazobenzene \\ Potassium \end{array} \longrightarrow \begin{array}{c} C_{g}H_{5}N < \stackrel{NO}{CH_{3}} \\ Methylphenyl-\\ nitrosamine \end{array} \longrightarrow \begin{array}{c} C_{g}H_{5}N < \stackrel{NH_{2}}{CH_{3}} \\ Unsym.-Methylphenyl-\\ hydrazine \end{array}$$

Phenylmethyl-nitrosamine, C₈H₈N(CH₂)NO, melts at 12-15° (B. 27, 365 Anm.). The methyl group is replaced by potassium when the substance is fused with caustic potash; potassium isodiazobenzene results.

Phenylethyl-nitrosamine, $C_8H_8N(C_2H_8)NO$, is a yellow oil with an odor like that of bitter almond oil (B. 7, 218).

Diphenyl-nitrosamine, (C₆H₅)₂NNO, melting at 66°, consists of pale yellow plates. It dissolves in concentrated sulphuric acid with a dark-blue color.

Nitrosoanilides.—Nitrosoformanilide, C₆H₅N(NO)CHO, melting at 39°, is produced when nitrous acid acts upon formanilide dissolved in glacial acetic acid. Nitrosoacetanilide, melting at 40°, recalls in its deportment the diazo-compounds. It is saponified by alkali to potassium diazobenzene. It yields diphenyl, with liberation of nitrogen, when it is treated with benzene. Potassium sulphite changes it to benzene diazosulphonic acid and phenylhydrazine disulphonic acid (p. 103) (B. 30, 366).

7. PHENYLNITRAMINES.

Diazobenzene Acid, Nitranilide, CaHaNH. NO2, or CaHaN: N.OOH, colorless

crystals melting at 46°, is formed:

(1) On oxidizing diazo- and isodiazo-benzene potassium with potassium ferricy-anide (B. 27, 2602), or with potassium permanganate (B. 28, R. 82); (2) by the nitration of aniline with nitrogen pentoxide (B. 27, 584; compare 29, 1015); (3) by decomposing diazobenzene perbromide with alkalies (B. 28, R. 31), together with nitrosobenzene (B. 27, 1273); (4) from nitryl chloride and aniline (B. 27, 668); (5) from aniline nitrate and acetic anhydride through the loss of water, just as in the case of acetanilide and aniline acetate. A series of other diazobenzene acids has been prepared by methods (2) and (5).

Properties and Behavior.—Diazobenzene acid is rearranged by light, by heat, and by contact with mineral acids into a mixture of o- and p-nitraniline (p. 93), with which it is isomeric. Sodium amalgam reduces it to isodiazobenzene sodium, and the latter with ease to phenylhydrazine (B. 27, 1181). Zinc and acetic acid convert it into diazobenzene. It forms salts. The potassium salt, C₆H₅N₅O₅K, and sodium salt, consist of white, glistening leaflets. Methyl iodide converts the sodium salt into the a-methyl

Phenylmethylnitramine, C₆H₅N<2, melting at 39°. The latter is changed by sulphuric acid to o- and p-nitromethyl aniline. It is converted into methyl aniline when heated with caustic potash. It can be reduced to methylphenyl-nitrosamine, unsym.-methylphenyl-hydrazine and monomethyl aniline. Methyl iodide converts the silver salt into β-diazobenzene methyl ester, CaHaN: NO, Q, CHa, a yellowbrown oil with an odor like heliotrope (B. 27, 359).

Homologous Diazobenzene Acids.—o-Diazotoluene Acid is a colorless oil. p-Diazotoluene Acid melts at 52° . Diazopseudocumene Acid melts at 87° . o-, m-, and p-Nitrodiazobenzene Acids melt at 65° , 86° , and 111° (B. 28, 399). Dinitrop-tolylmethylnitramine, $(NO_2)_2C_6H_2(CH_3)$. $N(CH_3)NO_2$, melting at 138° , has been prepared by the action of nitric acid upon dimethyl-p-toluidine (B. 29, 1015).

8. DIAZO-COMPOUNDS.

The aromatic diazo-derivatives, because of their ready conversion into the most varied substitution products of the aromatic hydrocarbons, and as intermediate steps in the formation of azo-dyes, are equally important both from a scientific and technical standpoint.

The behavior of the primary aliphatic amines toward nitrous acid was particularly emphasized in connection with them. As is known, the amido-group can, by this means, be replaced by hydroxyl; it is a change corresponding to that of ammonia itself by nitrous acid into nitrogen and water:

$$NH_3 + NOOH = H_3O + N_3 + H_2O$$

 $C_2H_5NH_2 + NOOH = C_3H_5OH + N_3 + H_3O$.

Among the nitrogen-containing derivatives of the aldehydo-acids we observed a body, in the reaction-product, resulting from nitrous acid and glycocoll ester, in which the group -N = N—had joined itself to carbon. This substance has been termed diazoacetic ester, produced according to the equation:

$$CO_2C_2H_5$$
. CH_2 . $NH_2 + NOOH = CO_2C_2H_5$. $CH(N_2) + 2H_2O$.

The moderated action of nitrous acid upon the salts of aromatic primary amines is analogous to its action upon aliphatic a-amido-acid esters. It was, however, observed long before the latter. When nitrous acid acts upon the aqueous solution of salts of primary aromatic amines without taking care to cool the mixture, there follows, as in the case of the aliphatic amines, a replacement of the amido-group by hydroxyl:

$$C_6H_5NH_2HCl + NOOH = C_6H_5OH + N_2 + H_2O + HCl.$$

Upon cooling the solution, however, the three hydrogen atoms will be replaced by a nitrogen atom, thus:

$$\begin{array}{lll} C_6H_5NH_3CI & + NOOH = C_9H_5NCI \equiv N & + 2H_3O \\ Diazobenzene Chloride & \\ C_6H_5NH_9ONO_2 & + NOOH = C_9H_5N(O\cdot NO_3) \equiv N & + 2H_3O \\ Diazobenzene Niisrate & \\ C_6H_5NH_9OSO_9H + NOOH = C_9H_5N(O\cdot SO_3H) \equiv N & + 2H_9O \\ Diazobenzene Sulphate. & \end{array}$$

These aromatic diazo-bodies differ from the aliphatic in that the bivalent group N₂ is linked not with both, but only with one affinity to the carbon atom. The second affinity is joined to another univalent radical. Bodies of this class, when boiled with water, yield oxy-compounds:

$$CO_{2}C_{2}H_{5}$$
. $CHN_{1} + H_{2}O = CO_{2}C_{2}H_{5}$. $CH_{2}OH + N_{2}$
 $C_{2}H_{5}N_{2}CI + H_{2}O = C_{2}H_{5}OH + HCI + N_{2}$

Formation of Diazobenzenes.—(1a) Gaseous nitrous acid, made by digesting arsenious acid with nitric acid, is conducted into a paste of the salt to be diazotized. The mixture is cooled all the while with ice. The solution of the diazo-compound is precipitated by a mixture of alcohol and ether. (1b) Add acid to the cooled solution of the salt to be diazotized sufficient (B. 8, 1073; 25, 1974 Anm.; 29, R. 1158) to liberate the nitrous acid from sodium or potassium nitrite, the well-cooled solution of which is gradually introduced into the acidified liquid:

$$C_8H_5NH_2$$
. $HCl + HCl + NO_2K = C_8H_5N_2Cl + 2H_2O + KCl$.

(2) As the diazobenzene salts are more freely soluble in water than in alcohol, in order to obtain solid diazo-salts the diazotizing, where practicable, should be made with alkyl nitrites (1, 144) dissolved in alcohol (15 parts of aniline, 150 parts of absolute alcohol, 20 parts of sulphuric acid, and 20 parts of amyl nitrite; B. 23, 2994; 28, 2048).

Sometimes a peculiar migration of the diazo-groups takes place on mixing the solution of an aniline salt with a diazo-salt solution. Thus, toluene diazochlorides and nitranilines (B. 29, 287) arise from nitrodiazobenzene chlorides and toluidines:

$$NO_2C_2H_4N_3Cl + C_2H_4(CH_3)NH_2 = NO_2 \cdot C_2H_4 \cdot NH_2 + C_2H_4(CH_2)N_2Cl$$

(3) Another procedure, occasionally applicable in diazotizing, consists in letting zincdust and hydrochloric acid act upon the nitrate of the diazo-derivative (B. 16, 3080):

$$C_a II_a$$
. NII_2 . $NO_2 H + Zn + 3HCl = C_a H_a$. $N_2 Cl + ZnCl_2 + 3H_2O$.

(4) By the action of hydroxylamine upon the nitrosobenzenes:

$$C_aH_aNO + H_aNOH = C_aH_aN : NOH + H_aO.$$

(5) Diazobenzene nitrate is precipitated upon conducting nitric oxide into a chloroform solution of nitrosobenzene (B. 30, 512):

$$C_6H_5NO + 2NO = C_6H_5N_2NO_3$$

- (6) By the saponification of nitrosoacetanilide with caustic alkali (p. 98).
- (7) By the action of mercuric oxide upon the phenylhydrazines (p. 120).
- (8) By allowing thionyl chloride, acetyl chloride, and other acid chlorides to act upon thionyl phenylhydrazone. The latter reacts in the form of diazobenzene-sulphoxyl, $C_aH_bN = NS(OH)$ (B. 270, 116):

$$C_6II_5N = NSOH + CH_5COCl = C_6H_5N_5Cl + S + CH_5 \cdot CO_5H$$
.

Properties.—The acid salts of the diazo-compounds are mostly crystalline, colorless bodies, which speedily brown on exposure to the air. They are readily soluble in water, slightly in alcohol, and are precipitated from the latter solution by ether. Consult B. 28, 1734, 2020, for their electric conductivity and cryoscopic behavior. They are generally very unstable (B. 24, 324) and decompose with a violent explosion when they are heated or struck a blow.

The diazo-derivatives are very reactive, and enter numerous, readily occurring reactions, in which nitrogen is liberated, and the diazo-group in the benzene nucleus directly replaced by halogens, hydrogen, hydroxyl, and other groups.

History and Constitution.—The diazo-compounds were discovered at the close of the '50s by Peter Griess (A. 137, 39), who regarded their salts as additions of $C_8H_8N_2$ and acids, e. g., HCl. Kekulé demonstrated that the azo-group only replaced one hydrogen of benzene, and held on the opposite side the radical of the acid, e. g., $C_8H_5 - N = N \cdot Cl$ (Z. f. Ch. N. F. (1866) 2, 308; Chemie der Benzolderivate I, 223). Blomstrand, A. Strecker, and E. Erlenmeyer, Sr., however, viewed the diazosalts as ammonium salts, e. g., $C_8H_5N(Cl) \equiv N$.

Proof of the fact that the azo-group N_2 replaces one benzene hydrogen atom is supposed to be found in the existence of such bodies as tetrabrombenzene-sulphanil-diazide.

Proof of the fact that the azo-group N_2 replaces one benzene hydrogen atom is supposed to be found in the existence of such bodies as tetrabrombenzene-sulphanil-diazide, $C_6Br_4 < \frac{N_2}{SO_3} > (B. 10, 1537)$. The relations of the diazobenzene salts to the hydrazines, (E. Fischer, A. 190, 100), and to the mixed azo-compounds argued in favor of Kekulé's

representation.

In recent years Blomstrand's formula has been accepted for the acid salts of the diazobodies (B. 29, R. 93, 783). Comparative studies of the cryoscopic behavior and the electric conductivity of diazo-salt solutions on the one side, and ammonium and alkali salts on the other (B. 28, 1734, 2020), have contributed to this assumption. The

diazo-salts are compared to the quaternary ammonium salts:

$$C_6H_5N:N$$
 $C_6H_5N:(CH_3)_9$,

and therefore are termed diazonium salts. From a chemical standpoint this view would indicate, among other things, the power of the diazonium haloids to form additive compounds with the halogens (p. 102)—a property which they would hold in common with quaternary ammonium halides (1, 168), as well as with certain alkali metals—e. g., caesium, rubidium. This formula also permits of the easy conversion of the aniline salts by means of nitrous acid into diazo-salts, without being compelled to assume, as is necessary in the Kekulé formula, the migration of the acid residue from the aniline nitrogen to the nitrogen atom which has but recently entered:

$$\label{eq:continuous_state} \begin{array}{l} C_{6}H_{5}NH_{3} \\ \overset{\cdot}{C}l \end{array} + NO_{2}H = \begin{array}{l} C_{6}H_{5}N \equiv N \\ \overset{\cdot}{C}l \end{array} + 2H_{2}O.$$

The hydrates corresponding to the diazonium salts are very unstable; they, however, yield metallic salts, $C_6H_6N_2OMe$, which can be handled. The diazoalkali salts are partially rearranged at the ordinary temperature, and partly on heating (B. 29, 455) into isodiazo-salts. The latter differ from the former in that they do not combine, or at least with difficulty, with aromatic amines or phenols to form dyes (Schraube and Schmidt, B. 27, 514). Inasmuch as these isodiazoalkali salts yield phenylmethyl-nitrosamines with methyl iodide (p. 98), while the normal diazo-salts form normal diazomethyl esters with methyl alcohol, the nitrosamine formula $-\epsilon$. g., C_6H_6NK . NO—was ascribed to the former. This view has not held true (B. 27, 1707), because, in acidylating, for example, with acid chlorides or anhydrides and sodium hydroxide, it is exactly the normal salts which afford nitroso-acid anilides, while the iso-salts are but slightly attacked by these reagents, and are in part reconverted into the normal salts (B. 30, 211). Bamberger viewed the normal diazo-bodies as derivatives of the real diazonium hydroxide, $C_6H_6N(OH)$: N, and left the Kekulé formula, C_6H_6N : NOH, for the iso-derivatives, as they were directly produced from nitrosobenzenes and hydroxylamine (p. 100). In the opinion of Hantzsch the isomerism of the diazobenzene alkali salts, in case of structural identity, is influenced by stereoisomerism (see benzaldoximes), corresponding to the following representations:

This last view allows of three classes of diazo-compounds; diazonium salts, syn- and

anti-diazo-compounds. The second and third are formed from and by a rearrangement of the first.

Isomeric series of diazobenzene sulphonic acids and diazocyanides have also been discovered.

I. Diazonium Salts.—Diazobenzene Chloride, C₆H₆NCl ≡ N, colorless needles (B. 23, 2996; 28, 2053). The platinum salt, [C₆H₆N₆Cl]₂PtCl₆, consists of yellow prisms. The gold salt, C₆H₆N₇Cl. AuCl₂ (A. 137, 52). Mercury salt, C₆H₆N₇Cl. HgCl₇, consists of white needles, decomposing at 122°. Diazobensene Bromide, C₆H₆. N₂Br, separates in white laminæ, if bromine be added to the ethereal solution of diazo-amidobenzene. Tribrom aniline remains in solution. Diazobensene Bromide Cuprous Bromide, CaH5N2Br. Cu2Br2, consisting of reddish-yellow needles, is decomposed by water into cuprous bromide, nitrogen, and brombenzene (p. 105) (B. 28, 1741).

Diazoperhalides.—The diazonium halides readily add two halogen atoms.

chloride of the ten combinations possible with the halogens, chlorine, bromine, and iodine, is the only one that has not been prepared. It may be remarked that the compound C₆H₅N₂BrICl can be both prepared as well from the chloride and BrI as from

the bromide and Cl I (B. 28, 2754).

Diazobenzene Perbromide, C₆H₅. N₂Br₃, is precipitated from the aqueous solution of diazobenzene nitrate or sulphate, by bromine in HBr-acid or NaBr. It is a dark-brown oil, which quickly becomes crystalline. It is insoluble in water and ether, and crystallizes from cold alcohol in yellow laminæ. Continued washing with ether converts it into diazobenzene bromide. It is changed by aqueous ammonia to diazobenzene imide Alkalies decompose it into nitrosobenzene and potassium diazobenzene (p. 111). (p. 98). Boiling alcohol converts it into brombenzene (p. 105).

Diazobenzene Nitrate, CaHaNO. NO2, consists of long, colorless needles which explode with greater violence than fulminating mercury or nitrogen iodide when they are

gently heated, struck, or subjected to pressure.

Diazobenzene Sulphate, C₄H₅. N₂. SO₄H, consists of colorless needles or prisms, which dissolve readily in water. It explodes at 100°. It is prepared either by diazotizing aniline sulphate or by allowing sulphuric acid to act upon diazobenzene nitrate (B. 28, 2049).

Oxalate (B. 28, 2059).

Carbonate, Nitrite, Acetate (B. 28, 1741).

Diazobenzene Sulphocyanide, CalloN, SCN, is a yellow, very explosive mass, obtained from diazobenzene chloride and potassium sulphocyanide. p-Chlordiazobenzene Sulphocyanide, CI[4]C₆H₄N₄. SCN, rearranges itself with ease into p-sulphocyan-diazo-benzene chloride, CNS[4]C₆H₄N₂Cl (B. 29, 947). p-Phenylenebisdiazo-chloride, C₆H₄(N₃Cl)₃, consists of yellow-colored, very explosive

needles (B. 30, 92).

2. Normal Diazohydrates are not known in a free state. In attempting to separate them by acids from their potassium salts, yellow-colored, exceedingly explosive and unstable precipitates are obtained under certain conditions. These appear not to be hydrates, but anhydrides—e. g., diazobenzene anhydride, $[C_0H_0N_2]_2O$; p-chlordiazobenzene anhydride, $[ClC_0H_4N_2]_2O$. These bodies redissolve in acids to diazonium salts, in alkalies to diazometallic salts, in ammonia to bisdiazoamido-bodies, and in anilines to

diazoamido-compounds (B. 29, 451).

Normal Diazobenzene Potassium, C₆H₅N₂OK, is produced on introducing a saturated aqueous solution of diazobenzene chloride into excessive and highly concentrated caustic potash (B. 29, 461). It forms white, pearly leaflets which can be quantitatively reconverted into diazobenzene chloride. It yields diazo-esters in the cold with alcohols (B. 29, 488): see B. 30, 339 for the reduction of potassium diazobenzene to phenylhydrazine. When alkaline diazobenzene solutions are oxidized with potassium ferricyanide or potassium permanganate the principal product is diazobensene acid (p. 98), together with a little nitrosobenzene (p. 66), nitrobenzene (p. 70), azobenzene (p. 112), and diphenyl. Benzoyl chloride and sodium hydroxide change normal potassium diazobenzene into nitrosobenzanilide, C₆H₅N(NO). CO. C₆H₅ (B. 30, 214). Salts of the heavy metals with diazobenzene are obtained by the precipitation of solutions of potassium diazobenzene with metallic salts (B. 23, 3035; 28, 226).

Diasobenzene Methyl Ether, CaH5N2. OCH2, isomeric with methylphenyl-nitrosamine

(p. 98), is obtained from normal or iso-diazobenzene silver and methyl iodide, as well as from diazobenzene potassium and methyl alcohol. It is a yellow, volatile oil, rapidly turning dark in color, possessing a penetrating, stupefying odor, and decomposing shortly after its liberation. Boiling dilute sulphuric acid decomposes it into nitrogen, methyl alcohol, and phenol (B. 28, 227). o- and p-Nitrodiazobenzene Methyl Ether, NO, .- $C_6H_4N_2$. OCH₃ (B. 28, 236). Di-p-nitrophenyldiaso-sulphide, $[NO_2[4]C_6H_4N_2]_2S$, is precipitated as an egg-yellow, very explosive mass, on adding hydrogen sulphide to a neutral solution of the diazo-chloride. With benzene it forms nitrodiphenyl, nitrogen, and sulphur; di-p-nitrodiphenyl disulphide is formed simultaneously. In an acid solution with an excess of hydrogen sulphide there is produced, along with the diazosulphide, p-nitrophenyldiazomercaptan hydrosulphide, NO₂. C₈H₄N₂SH_. SH₄, consisting of red, brilliant, metallic-looking needles, which dissolve with a deep-red color in the They decompose, when fused, with the formation of nitrophenylhydrazine, nitraniline, sulphur, and dinitrophenyl disulphide. Non-explosive Di-p-nitrophenyldiazodisulphide, [NO₂C₆H₄N₂]₂S₂, is finally the third product in the action of hydrogen sulphide. It is insoluble in alkali. It consists of sulphur-yellow needles, soluble in acetone (B. 29, 272). See thiophenol for diazobenzene thiophenyl ether.

3. Isodiazohydrates are liberated from their potassium salts by acetic acid. They are very easily decomposed. Those of benzene and toluene are colorless oils. p-Nitro-

isodiazobensene hydrate, NO₂. C₆H₄N₄OH (B. 29, 1383), has been analyzed.

Potassium Isodiazobensene, C₆H₅N₂OK, is formed on digesting potassium diazobenzene for a brief period at 130-135° with concentrated caustic potash, and when fused, caustic potash acts upon phenylmethyl-nitrosamine (p. 98), into which it returns upon treatment with methyl iodide (B. 27, 514, 672, 680). Sodium amalgam reduces it with ease to phenylhydrazine (B. 29, 473; 30, 339). Potassium Iso-p-diazotoluene results when its isomeride lies exposed to the air (B. 29, 1385). Iso-p-nitrodiazotoneene sodium, C₆H₄(NO₃)N₂ONa + 2H₂O, yields nitrophenylmethyl-nitrosamine with methyl iodide, whereas the silver salt forms the corresponding diazo-ester (B. 29, 1384).

Diszobenzene Sulphonic Acid Register appropriate Acid C H N SO H is very

Diazobenzene Sulphonic Acid, Bensene-asosulphonic Acid, CaH, N, SO, H, is very decomposable (B. 30, 75). Its potassium salt is produced upon introducing diazobenzene nitrate into a cold, neutral, or feebly alkaline solution of dipotassium sulphite; the liquid solidifies to a yellow, crystalline mass. Under other conditions a more easily decomposable, orange-colored salt is formed (B. 27, 1715, 2930). For the sensitivity of the diazobenzene sulphonates to light and their application in photography consult B. 23, 3131. Monopotassium sulphite reduces diazobenzene nitrate to potassium phenylhydrazine sulphonate (p. 119), which mercuric oxide oxidizes to potassium diazobenzene sulphonate (B. 27, 1245).

p-Nitrodiazobenzene nitrate and one molecule of KaSOs yield potassium p-nitrodiazobenzene sulphonate, which also appears to exist in two forms. The acid crystallizes with four molecules of water in ruby-red prisms (B. 30, 90). On using two molecules of potassium sulphite the product is potassium p-Nitrophenylhydrasine disulphonate, C6H6(NO2)N(SO3K)NH . SO3K (p. 125) (B. 29, 1829). p-Chlor- and p-Brombenzene

Diazosulphonic Acid (B. 30, 75).

The diazonium salts and benzene sulphinic acid combine to Benzene diazosulphones, C₆H₅N₂SO₂C₆H₅, which are resolved by hydrochloric acid into diazonium chlorides and sulphinic acids (B. 30, 312).

Diazobenzene Cyanide, C₆H₅N₂CN, appears as an unstable oil, on adding a potassium cyanide solution to the solution of a diazobenzene salt. If, however, the reverse be done—the diazo-salt be added to the potassium cyanide solution—a prussic acid additive product, C₈H₈N₂CN. HCN, will separate as a yellow precipitate, melting at 70°. Bensenediasocarbonamide, phenylazocarbamide, C₈H₅N: NCONH₂, results from the oxidation of phenylsemicarbazide (p. 127) (J. ch. Soc., 1895, I, p. 1067; B. 28, 1925, 2599). It consists of reddish-yellow needles, melting at 114°. The anilide, C₈H₅N₂-CONHC₈H₈, from diphenylsemicarbazide (B. 29, 1691), melts at 122°.

Two isomerides have been obtained from p-chlor- and p-nitrodiazobenzene cyanide, and in each instance the one body is unstable and the other stable. The unstable, lowmelting modifications only form at lower temperatures, decompose easily, especially in contact with copper powder (p. 105), give up nitrogen with the formation of benzene cyanides, form azo-dyes with aromatic amines or phenols, and change rapidly, particularly in alcoholic solution, into the stable isomerides. Unstable p-cklor- and p-mitro-diasobensene cyanide, melt at 28° and 29°; stable p-cklor- and p-nitro-diasobensene cyanide melt at 106° and 86°. The stable cyanides unite to diazocarbonamides with water, and with alcohols to imide ethers, from which the potassium salts of the corresponding diazobenzene carboxylic acids can be obtained by saponification. The acids themselves are very decomposable (B. 28, 670, 2072). Tribromphenylazocarboxylic Acid, $C_6H_2Br_5$. N_2 . COOH, has been obtained from its amide, the oxidation product of tribromphenylaemicarbazide (B. 28, 1929).

The Most Important Decompositions of the Diazobenzene Salts.—The decompositions of the diazo-salts in which nitrogen is evolved and atoms of other non-metals or atomic groups enter and take its place are of the greatest importance for the genetic relations of very many of the most varied di- and polysubstitution products of benzene and its homologues (p. 38).

(1) Replacement of the Diazo-group by Hydrogen:

(a) If the salts be boiled with strong alcohol, then hydrogen will enter for the diazo-group, and hydrocarbons result. The alcohol is oxidized to aldehyde (A. 137, 69; 217, 189; B. 9, 899);

$$C_0H_0 \cdot N_2 \cdot HSO_4 + C_2H_0O = C_0H_0 + N_2 + SO_4H_2 + C_2H_4O$$
.

It has occurred upon boiling with alcohol that the diazo-group was not replaced by hydrogen, but by oxy-ethyl (O. C₂H₆), with the production of phenol ethers (B. 17, 1917; 18, 65; 26, R. 547). If the dry diazo-salt be decomposed with alcohol, phenol ethers

are the chief products (B. 21, R. 99; 22, R. 657).

(b) The replacement of the diazo group by hydrogen is sometimes effected by its conversion into the hydrazine derivative and then boiling this with copper sulphate or ferric chloride (see phenylhydrazine). The reaction taking place on boiling the diazochlorides with a stannous chloride solution is, in all probability, dependent upon the intermediate formation of hydrazines (B. 22, R. 741):

$$C_6H_4(C_4H_9)$$
. $N_2Cl + SnCl_2 + H_2O = C_6H_5(C_4H_9) + N_2 + SnOCl_2 + HCl.$

(c) An analogous procedure for the replacement of the diazo-group by hydrogen consists in dissolving the diazo-compound in caustic soda and adding a solution of stannous oxide in sodium hydroxide (B. 22, 587). Diphenyl derivatives frequently appear as secondary products.

(d) The diazides of sulphonic acids can be boiled with copper powder and formic

acid (B. 23, 1632).

(2) Replacement of the Diazo-group by Halogens:

(a) The diazobenzene salts are treated with haloid acids. Hydriodic acid of the four acids of this class reacts most readily:

$$C_6H_5N_2.OSO_2H + HI = C_8H_5I + N_2 + SO_4H_9.$$

The haloid acids are frequently applied in glacial acetic acid solution.

The hydrobromides or hydroiodides of the bases can also be treated with nitric acid.

(b) Concentrated haloid acids are allowed to act upon the diazoamido-derivatives (p. 109). This reaction is especially recommended for the preparation of fluor- or chlor-derivatives (B. 21, R. 97):

$$C_aH_aN = N \cdot NH \cdot C_aH_a + 2HF = C_aH_aF + N_a + FH \cdot NH_a \cdot C_aH_a$$

(c) Chlor- and brom-derivatives are formed, if the PtCl₄- and PtBr₄-double salts are heated alone; or, what is better, with dry soda or salt:

$$(C_aH_a \cdot N_aCl)_a \cdot PtCl_4 = 2C_aH_aCl + N_2 + 2Cl_2 + Pt.$$

(d) When the diazo-perbromides are boiled with alcohol (the latter is oxidized to aldehyde), brombenzenes are formed:

$$C_{e}H_{b}$$
. N_{2} . $Br_{s} + CH_{2}CH_{2}OH = C_{e}H_{b}Br + N_{2} + 2HBr + CH_{3}$. CHO.

The reactions indicated under a, b, c, and d were all observed by P. Griess. Another reaction belongs in this group: it was discovered by Sandmeyer (B. 17, 2650; 23, 1880), and is capable of far greater generalization. It is based upon the fact that diazo-salts are decomposed by cuprous salts:

(e) When cuprous chloride is added to an aqueous solution of diazobenzene chloride, an additive product, C₆H₅N₂Cl. Cu₂Cl₂, is formed at first, but upon the application of heat this decomposes into C₆H₅Cl (B. 19, 810; 23, 1628; A. 272, 141):

$$C_aH_aN_aCl(Cu_aCl_a) = C_aH_aCl + N_a + Cu_aCl_a$$

Cuprous bromide and cuprous iodide act similarly upon the corresponding diazobenzene salts.

A modification of the method consists in treating the diazo-derivatives in the presence of hydrochloric, hydrobromic, or hydriodic acid with copper powder (B. 22, 1218; 25, 1001 Anm.).

copper powder (B. 23, 1218; 25, 1091 Anm.).

(3) Replacement of the Diazo-group by Hydroxyl.—When the salts (sulphates are best) are boiled with water, the diazo-group will be replaced by hydroxyl:

$$\begin{array}{lll} C_0H_6 \cdot N_2 \cdot Br & + H_2O = C_0H_6 \cdot OH + N_2 + HBr \\ C_0H_6 \cdot N_2 \cdot NO_3 + H_2O = C_0H_6 \cdot OH + N_2 + NO_2H \\ C_0H_6N_2SO_4H & + H_2O = C_0H_6OH & + N_2 + SO_4H_2. \end{array}$$

Nitro-phenols appear as side products in the decomposition of the diazonitrates. It was mentioned upon p. 104 that in the action of alcohol upon diazo-salts alkyl phenol ethers are formed, together with the hydrocarbons; similar products are observed when phenol (B. 23, 3705), glacial acetic acid (B. 21, R. 889), and acetic anhydride (A. 235, 234) are used

(4) Replacement of the Diazo-group by the Sulphydrate Group.—On digesting the diazide of sulphanilic acid (see this), a cyclic diazo-salt, with alcoholic potassium sulphide, the potassium salt of p-thiophenolsulphonic acid will be produced (B. 20, 350):

In the same manner, when mercaptan acts upon diazobenzenesulphonic acid, a compound results which, upon standing or warming, decomposes into thiophenolethylether-p-sulphonic acid:

$$C_{\mathfrak{g}}H_{\mathfrak{4}} < \stackrel{N_{\mathfrak{g}}}{SO_{\mathfrak{g}}} > \longrightarrow C_{\mathfrak{g}}H_{\mathfrak{4}} < \stackrel{N_{\mathfrak{g}}SC_{\mathfrak{g}}H_{\mathfrak{5}}}{SO_{\mathfrak{g}}H} \longrightarrow C_{\mathfrak{g}}H_{\mathfrak{4}} < \stackrel{SC_{\mathfrak{g}}H_{\mathfrak{5}}}{SO_{\mathfrak{g}}H}.$$

The xanthates yield aromatic xanthogenic esters,—e. g., C₈H₅S. CSOC₂H₅,—which, upon saponification, yield thiophenols (J. pr. Ch. [2] 41, 184). The formation of di-p-nitrophenyldisulphide by the decomposition of the corresponding diazosulphide and mercaptan has already received mention (p. 103).

- (5) Replacement of the Diaso-group by the Nitro-group.—This may be accomplished by adding the diazobenzene nitrite solution to freshly precipitated cuprous oxide (B. 20, 1495; **23,** 1630).
- (6) Replacement of the Diazo group by the Cyanogen Group.—This reaction connects by easy stages the nitroamidobenzenes with the nitrobenzoic acids, and the latter with the phthalic acids. The importance of this fact has received mention (p. 38). Add the diazobenzene chloride solution to a copper sulphate solution mixed with potassium cyanide (B. 20, 1495; 23, 1630) (compare p. 103):

$$C_8H_6N_2CN = C_8H_6CN + N_9$$

(7) Sulphocyanides (Rhodanides) result when the diazo-salts are boiled with potassium and cuprous sulphocyanides (B. 23, 770).

(8) When a solution of diazobenzene sulphate is mixed with potassium cyanate and reduced copper is then added (B. 25, 1086), phenylisocyanide or carbanile will result

(9) Formation of Diphenyl Compounds from Diaso-derivatives.—Diphenyl derivatives frequently appear as side products in the treatment of diazo-bodies with reducing agents —c. g., stannous chloride (B. 18, 965), alcohol, and reduced copper (B. 23, 1226), alcohol alone or sodium ethylate (B. 28, R. 389)—as well as in the action of water, of phenol (B 23, 3705), and of potassium ferricyanide (B. 26, 471). Into aromatic hydrocarbons and heterocyclic compounds—e.g., thiophene, pyridine, and quinoline—diazobenzene chloride introduces the phenyl group. This occurs very easily in the presence of aluminium chloride (B. 26, 1994):

$$C_aH_5N_2Cl + C_aH_a \xrightarrow{Al_2Cl_4} C_aH_5C_aH_5 + N_2 + HCl.$$

The diazo-residue in the diazo-oxides, diazo-sulphides, and isodiazohydrates is readily replaced by cyclic residues (B. 28, 404; 29, 165, 274, 452):

Other Reactions of Diazo-derivatives, in which nitrogen is not set free. 1. Phenylhydrazines are produced in the reduction of diazo-salts

(p. 119).

2. When diazo-compounds are oxidized in alkaline solution, they are converted into nitrosobenzene (p. 70) and phenylnitroamine or diazobenzene acid (p. 98).

3. The behavior of diazo-bodies toward ammonia, alkylamines, aniline, and related bases, when diazoimido- (p. 110), diazoamido- (p. 107), and mixed azo-derivatives arise, is worthy of special note. These very important reactions will be given in detail, with the individual classes.

4. Hydrazones result when diazobenzene in alkaline solution acts upon bodies containing the group CH2. CO (p. 121). The primarily formed hydrazones often rearrange themselves with additional quantities of the diazobenzene salt into formazyl derivatives, which belong to the class of amidines (1, 270) (B. 27, 147, 320, 1679; 29, 1386).

g. DIAZOAMIDO-COMPOUNDS. 10. DISDIAZOAMIDO-COMPOUNDS.

The diazoamido-compounds are derived from the unknown hydride NH = N-NH₂, in which the hydrogen of the imide group is replaced by an aromatic residue—e. g., phenyl, tolyl, etc.—and the hydrogen of the amido-group by aliphatic or aromatic residues: mixed and true aromatic diazoamido-compounds. The disdiazoamido-bodies are also derivatives of an unknown nitrogen hydride, NH = N - NH - N = NH.

Formation of Diazoamido-derivatives.—They result from the transposition of primary and secondary amines with diazo-salts: (1 a) Primary aromatic amines yield diazoamido- or disdiazoamido-bodies, depending upon the conditions of experiment. Diazoamido-compounds are formed when equimolecular quantities of diazo-salt and primary amine interact:

$$C_6H_5N_2$$
. $Cl+NH_1$. $C_8H_5 = C_6H_5N = N - NHC_6H_5 + HCl$.

They are also produced when an alkali nitrite, in the absence of mineral acids, acts upon the salts of primary amines:

$$2C_6H_5NH_2HCl + NO_2K = C_8H_5N = N - NH \cdot C_6H_5 + KCl + HCl + 2H_2O.$$

(1b) A disdiazo-compound results if a molecule of aniline be allowed to act in alkaline, alcoholic solution upon two molecules of a diazobenzene salt. It can also be obtained by transposing diazobenzene chloride with diazoamidobenzene (B. 27, 703):

When a diazobenzene salt solution is allowed to flow into cold, concentrated ammonia, disdiazobenzeneamide, C₆H₅N: N. NH. N: NC₆H₆ (B. 28, 171), will be produced.

Course of the Reaction in the Formation (1a) of Diazoamido-derivatives.—It is an interesting fact that the same diazobenzene-p-amidotoluene is formed, e. g., from diazobenzene chloride and p-toluidine, as from diazo-p-toluene chloride and aniline, although different compounds might well have been expected:

$$\begin{array}{l} C_0H_5N_2CI + NH_2[4]C_0H_4[1]CH_3 \longrightarrow & I. \ \ C_0H_5N = N - NH[4]C_0H_4[1]CH_3 \\ CH_2[1]C_0H_4[4]N_2CI + NH_2C_0H_5 \longrightarrow & II. \ \ CH_2[1]C_0H_4[4]N = N - NH . \ \ C_0H_6. \end{array}$$

This behavior would justify the assumption that the same intermediate product is formed in both instances by the addition of the primary base with simultaneous breaking down of the double nitrogen union:

$$C_6H_5NH - NCl - NH[4]C_6H_4[1]CH_3$$
.

The same compound can then result if hydrochloric acid be eliminated, it being immaterial from which bodies the synthesis began (B. 14, 2447; 21, 3004). Hence, the decomposition of a diazoamido-body by an haloid acid cannot be used in ascertaining its constitution, because the haloid acid would first form an addition product. For this purpose phenylisocyanide seems better adapted. Thus, diazobenzene-p-amidotoluene forms a urea with this reagent, and this new compound will have either formula I', corresponding to I, or II', corresponding to formula II, depending upon the constitution of the diazoamido-body:

$$\begin{array}{c} \text{NH . C}_{6}^{H_{5}} \\ \text{IV : } \text{CO} < NH . C}_{N < [4]}^{C_{6}} \\ \text{H}_{5}^{[1]} \text{CH}_{5} \\ \text{NH . C}_{6}^{H_{5}} \\ \text{NH . C}_{5}^{H_{5}} \\ \text{IIV . } \text{CO} < NH . C}_{N < [4]}^{C_{6}} \\ \text{NH . C}_{6}^{H_{5}} \\ \text{IIV . } \\ \text{CO} < NH . C}_{N < [4]}^{H_{5}} \\ \text{CO} < NH . C}_{NH . C}^{H_{5}} \\ \text{CO} < NH . C}_{NH . C}^{$$

On decomposing the urea with dilute sulphuric acid the products will be phenyl-ptolyl urea, phenol, and nitrogen; whereas, according to formula II', they should be sym. diphenylurea, p-cresol, and nitrogen. Therefore, diazobenzene-amido-p-toluene is constituted according to formula I. The imide group apparently combines with the more negative radical (H. Goldschmidt, B. 21, 2578). Granting the diazonium formula for the diazo-salts, it will of course be necessary to alter the preceding explanation somewhat.

The normal diazo-alkali salts (p. 102) also yield diazoamido-derivatives. Consult B. 29, 289, for the occurring changes. The isodiazo-salts, resulting from rearrangement of

the normal salts, are not reactive.

- (16) Primary aliphatic amines also yield diazoamido- and disdiazoamido-bodies (B. 22, 934). (10) Secondary aliphatic amines form mixed fatty-aromatic diazo-amido-derivatives (B. 8, 148, 843).
- 2. Diazoamido-compounds are also formed in the action of free nitrous acid upon the alcoholic solutions of free primary amines; the free diazobenzene hydrate or anhydride produced at first (p. 102) is transposed by aniline:

$$C_6H_5N_2$$
. OH + NH₂. C_6H_5 = C_6H_5N = N-NH. C_6H_5 + H₂O.

The action of nitrites—e.g., silver nitrite upon free aniline—produces salts of diazo-amido-bodies, $C_6H_5N_2$. NAg C_6H_6 (B. 29, R. 1158).

3. They can also be obtained by the action of the nitrosoamines upon the primary amido-bodies. Phenylmethylnitrosamine and aniline yield diazoamidobenzene:

$$\overset{C_6H_5}{\underset{CHI_8}{\text{CH}_5}} > \text{N. NO} + \text{NH}_{\text{2}}. \\ C_6H_6 = \overset{C_8H_6}{\underset{CHI_8}{\text{CH}_5}} > \text{N. N}: \text{N. } C_6H_6 + \text{H}_{\text{2}}\text{O}.$$

Nitrosoacetanilide (p. 98) and aniline also react, the products being diazoamido-benzene and acetic acid. When one molecule of aniline is used with two molecules of nitrosoacetanilide, and these bodies are allowed to react in alkaline solution, an aromatic disdiazoamido-compound is produced:

Diazoamido-compounds from primary, aromatic bases.

Diazo-amido-benzene, Benzenediazoanilide, Diazobenzeneanilide (B. 14, 2443 Anm.), C₆H₆. N₂. NH. C₆H₅, melts at 96° and explodes when it is heated to higher temperatures. It is obtained by the action of nitrous acid on the cold alcoholic solution of aniline (Griess, A. 121, 258); by mixing diazobenzene nitrate with aniline (B. 7, 1619); and by pouring a slightly alkaline sodium nitrite solution upon aniline hydrochloride (B. 8, 1074) or sulphate (B. 17, 641; 19, 1953; 20, 1581).

Diazo amidobenzene consists of golden-yellow, shining laminæ or It is insoluble in water, sparingly soluble in cold, but readily in hot alcohol, ether, and benzene. Its transpositions will be discussed later; the most remarkable one is its rearrangement into isomeric amido-

azobenzene (p. 115).

Its salts are very unstable, although it forms a double salt $(C_{12}H_{11}N_3 . HCl)_3$. $PtCl_4$, with hydrochloric acid and $PtCl_4$. It crystallizes in reddish needles. When the alco-

holic solution is mixed with silver nitrate, the compound, CaHs. NaNAg. CaHs, separates in reddish needles.

Sodium in ethereal solution converts it into CaHaNNaN = N. CaHa, which is decom-

posed by water (B. 27, 2315). Benzene diasoacetanilide, $C_gH_bN=N-N(COCH_s)C_gH_b$, melts with decomposition at 130°, and is formed when diazo-amido benzene stands with acetic anhydride in toluene solution (B. 24, 4156).

The para-variety of the three diaso-amido toluenes is alone stable. The ortho- and meta-forms (from ortho- and meta-toluidine) immediately pass into isomeric amido-azo-

Diazo-amido-compounds containing two different aromatic residues: Mixed diazoamido-compounds, like diasobensene-p-amidobrombenzene, melting at 91° (B. 20, 3012), o-, m-, p-Dinitrodiasoamido-bensene, melting at 196°, 194°, 228° (B. 27, 2201; 28, R. 303), diazobensene-p-amidotoluene, can be obtained from the diazo-derivatives of the two components with the free amido-derivatives-e.g., diazobenzene-p-amidotoluene equally well from the diazobenzene salt with p-toluidine, as from p-diazotoluene salt and aniline.

The explanation of this peculiar behavior is given on page 107.

Disdiazobenzene Amide, $(C_8H_5N:N)_2NH$ (B. 27, 899), is extremely decomposable.

Disdiazobenzene Anilide, $C_8H_5N=N-N(C_8H_5)-N=NC_8H_5$, consists of shining yellow leaflets, which explode at 80-81° in a capillary tube (B. 27, 703).

Mixed fatty-aromatic Diazoamido-compounds

Diasobenzene-ethylamine, $C_6H_6N=N-NH$. $C_2H_6(?)$, is a yellow oil. Diasobenzene-dimethylamine, $C_6H_6N=N-N(CH_3)_2$, is a yellow oil (B. 8, 148). Diasobenzene-piperidine, $C_6H_6N=N-NC_8H_{10}$, melts at 43°. The diazopiperidines are of practical value in the preparation of fluorine derivatives (p. 58) which results were noticed with the properior of the sult upon acting with concentrated hydrofluoric acid upon them (A. 235, 242; 243, 223). Disdiasobensene-methylamine, (C₆H₅N = N)₂NCH₃, consists of bright yellow needles,

melting at 112°. Disdiazobenzene-ethylamine melts at 70° (B. 22, 934).

The Rearrangements of the Diazoamido-compounds.—(1) The most remarkable property of the diazoamido-compounds containing a replaceable hydrogen atom in the p-position with reference to the NHgroup, is their ability to rearrange themselves into isomeric p-amidoazoderivatives. In the amidoazo-body the amido-group holds the p-position with reference to the point of union (p. 115):

$$C_8H_5N = N-NHC_8H_5 \longrightarrow C_8H_5N = N[1]C_8H_4[4]NH_2.$$

This rearrangement completes itself in the course of a few days, when a small quantity of an aniline salt is present. It may be assumed that in the conversion a quantity of aniline, equal to that actually needed for the change, is produced; consequently a comparatively small amount of the aniline salt will be sufficient to rearrange a large quantity of diazoamido-benzene into amido-azobenzene (Kekulé, Z. f. Ch. (1866), 689; B. 25, 1376). The rapidity of the conversion is proportional to the strength of the acid, whose aniline salt is employed (B. 29, 1899). strong base, such as amidoazobenzene, is obtained from a body indifferent to acids—e. g., diazoamidobenzene. Various intramolecular atom-rearrangements, such as the preceding, in which indifferent compounds are rearranged to strong bases or strong acids are known—e. g., the rearrangement of hydrazobenzene into benzidine, of benzil into benzilic acid, etc. (1, 54; 11, 116, 118).

(2) The imide hydrogen of the diazoamidobenzene can be replaced by acid radicals through the action of acid anhydrides (see benzene

diazoacetanilide).

(3) The diazoamido-compounds and phenylisocyanate combine to urea derivatives. Consult p. 108 upon the importance of this reaction.

In the preceding reactions the diazoamido-bodies are not decomposed. This occurs very readily (4) on treating them with concentrated haloid acids; the diazoamido-derivatives, like the diazobenzene salts, then change to haloid benzenes; the side products are salts of the bases previously in combination with the diazo-residue. Therefore, the diazoamido-compounds, in the presence of acids, are fully converted by nitrous acid into diazobenzene salts. The deportment of the diazo-amido-bodies toward concentrated hydrofluoric acid with the addition of diazopiperidines, proved itself particularly well adapted for the preparation of fluor-benzenes (A. 243, 220):

$$C_6H_5N = N - NC_5H_{10} + 2HFI = C_6H_5FI + N_2 + HFI. HNC_5H_{10}$$

- (5) Boiling water converts the diazoamido-compounds into phenols and bases.
- (6) The reduction of the diazoamido-bodies has not led to hydrazoamido-derivatives—e. g., C₆H₈NH — NH. NH. C₆H₅; a decomposition into phenylhydrazine and aniline has been the usual result.
- (7) On boiling the alcoholic solution with sulphurous acid, the diazogroup is replaced by the sulpho-group:

$$C_6H_5.\ N_2.\ NH.\ C_6H_5+2SO_2+2H_2O=C_8H_5.\ SO_3H+N_2+NH_2.\ C_6H_5.\ SO_3H_2.$$

II. DIAZO-OXYAMIDO-COMPOUNDS.

These compounds result from the interaction of diazo-bodies with alkyl- and alphyl-hydroxylamines.

Diazo-oxyamido-benzene, $C_8H_5N_2$. $N(OH)C_8H_5$, melting at 127°, consists of yellow, silky needles. It is formed as well from nitrosobenzene and phenylhydrazine, as from diazobenzene and phenylhydroxylamine. p-Nitrobenzene-diazoxyamido-methane, $NO_3C_8H_4N_2N(OH)CH_3$, melts at 228° (B. 29, 103).

12. DIAZOIMIDO-COMPOUNDS.

The diazoimido compounds are ethers of hydronitric acid—hydrazoic acid. They are produced:

(1) By the action of aqueous ammonia upon diazobenzene perbromides:

$$C_6H_5$$
. N_3 . $Br_3 + NH_3 = C_6H_6$. $N < N + 3HBr$.

(2) By the action of hydroxylamine upon diazobenzene sulphate (B. 25, 372; 26, 1271):

$$C_6H_5$$
. N_4 . $SO_4H + NH_2OH = C_6H_5$. $N_3 + H_4O + SO_4H_4$.

(3) By the action of sodium nitrite upon the hydrochloric acid solution of phenylhydrazine, when the nitrosophenylhydrazine first produced sustains decomposition:

$$C_6H_5$$
. $N <_{NO}^{NH_2} = C_6H_5N <_N^N + H_2O$.

(4) From phenylhydrazine and diazobenzene sulphate (B. 20, 1528; 21, 3415):

 $C_aH_aN: N.NH.NH.C_aH_a = C_aH_aNH_a + C_aH_bN_a$

(5) Hydrazine and diazobenzene sulphate yield, on the one hand, diazobenzene imide and ammonia, upon the other, aniline and azoimide or hydronitric acid as side products. These reactions are due to the breaking-down of a non-accessible intermediate product, C₆H₅N = N -NH. NH₂ (B. 26, 88, 1271) (compare buzylene derivatives, p. 131):

Diazobenzene Imide, Phenylhydronitric Ester, C. H. N., boiling at 59° (12 mm.), is a yellow oil with stupefying odor. It explodes at the ordinary pressure if heated.

o-Nitrodiazobenzene Imide, NO2CaH4N2, melts at 52°. m-Nitrodiazobenzena Imide melts at 55°. p-Nitrodiazobensene Imide melts at 74°.

Transformation of the Diazobenzene-imido-compounds.—(1) They are decomposed

into N₃ and chloranilines when boiled with hydrochloric acid (B. 19, 313).

(2) They break down, when boiled with sulphuric acid, into nitrogen and amidophenols (B. 27, 192).

(3) The diazobenzene imide compounds, nitrated in the o- and p-positions, decompose in part when boiled with alcoholic potash into nitrophenols and hydrazoic acid (B. **25**, 3328).

13. AZOXY-COMPOUNDS.

Formation.—(1) By reduction of nitro- and nitroso-compounds with methyl or ethyl alcoholic potash solutions (B. 26, 269):

$$4C_8H_5NO_2 + 3HCH_2ONa = 2(C_8H_5N)_2O + 3HCO_2Na + 3H_2O.$$

Sodium amalgam and alcohol, zinc dust in alcoholic ammonia, and arsenious acid in alkaline solution (B. 28, R. 125) reduce nitro-bodies to azoxy-compounds.

(2) By the oxidation of amido- and azo-derivatives (Z. f. Ch. (1866) 309; B. 6, 557; 18, 1420), as well as by the spontaneous oxidation of

 β -phenylhydroxylamine (p. 70) in the air.

Deportment.—1. When reduced by heating with iron filings they yield azo-compounds, with ammonium sulphide hydrazo-derivatives, and with acid reducing agents amido-bodies, resulting from the decomposition and rearrangement of the hydrazo-compounds first produced. 2. Their rearrangement into oxy-azo-compounds, on digesting them with concentrated sulphuric acid, is interesting (Wallach and Belli, B. 13, 525).

Azoxybenzene, Azoxybenzide, $C_6H_6-N \stackrel{\bigcirc}{\longrightarrow} N - C_6H_6$, forms long, yellow needles, easily soluble in alcohol and ether, but not in water. It melts at 36°, and decomposes into azobenzene and aniline when distilled. It is converted into p-oxyazobenzene by digestion with concentrated sulphuric acid.

sym.-m-Dinitroazoxybenzene, from m-dinitrobenzene (B. 25, 608), melts at 141°. sym.-m-Diamidoasobenzene, Azoxyaniline, melts at 147° (B. 29, R. 137).

p. Tetramethyldiamido azoxybenzene, from nitrosodimethyl aniline, melts at 243°. Tri-

nitroasoxybensenes are obtained from azoxybenzene (B. 23, R. 104).

o-Azoxytoluene melts at 59°. m-Azoxytoluene melts at 38°. p-Azoxytoluene melts at 70°.

14. AZO-COMPOUNDS.

Like the diazo-derivatives, these contain a group, consisting of two nitrogen atoms; in the former the N₂-group is combined with only one benzene nucleus and an inorganic residue; here it is attached on either side to benzene nuclei, or to a benzene nucleus and an aliphatic radical:

$$C_eH_5-N=N-C_eH_5$$
 $C_eH_5-N=N-CH_3$ Azobenzene Benzene Azomethane.

In consequence, they are far more stable than the former, and do not react with the elimination of nitrogen.

Classification and Nomenclature.—The true aromatic azo-bodies are distinguished as symmetrical, those in which the two residues are the same, and unsymmetrical, those in which the two residues are dissimilar. Mixed azo-bodies are those in which the azo-group joins an aromatic to an aliphatic radical.

The names of the unsymmetrical azo-bodies are derived from the names of the two bodies in which the azo-group has replaced an atom of hydrogen each, separated by the word azo,—thus: $C_6H_5-N=N-C_6-H_4N(CH_3)_2$, benzene azo-dimethyl aniline; $C_6H_6-N=N-CH_3$, benzene azomethane. Should the benzene residues contain substituents, the positions in the one residue are indicated with numbers 1 to 6, and in the second residue by numbers 1' to 6', with the understanding that the azo-group occupies the 1,1'-position.

Disazo- and trisazo-compounds, containing two or three azo-groups,

are known (B. 15, 2812).

Formation.—1. By the moderated reduction of nitro-bodies in alkaline solution, because in acid solution the final reduction products of nitro-bodies, the amido-derivatives, are almost invariably produced. Azoxy-compounds are first formed, but by further reduction they pass into azo-derivatives. The reducing agents are:

(a) Zinc-dust in alcoholic potash or soda (B. 21, 3139), or in ammo-

nia;

(b) Sodium amalgam and alcohol;

(c) Stannous chloride in sodium hydroxide (B. 18, 2912).

By more complete reduction hydrazo-bodies are formed, along with the azo-derivatives; these can eventually be decomposed into amido-compounds. Azobenzene is the middle member in the series of reduction products obtained from nitrobenzene, if β -phenylhydroxylamine is not taken into consideration:

$$\begin{array}{c} C_{\mathbf{c}}H_{\mathbf{5}} \cdot NO_{\mathbf{2}} \longrightarrow C_{\mathbf{c}}H_{\mathbf{5}} \cdot N \longrightarrow C_{\mathbf{c}$$

- 2. By reduction of azoxy-compounds on heating them with iron
- 3. By the oxidation (a) of hydrazo-bodies (p. 116), and (b) of primary amido-derivatives in alkaline solution with potassium permanganate (A. 142, 364) or with potassium ferricyanide.
 - 4. By the action of nitrosobenzene (p. 70) upon aniline.
- 5. By the rearrangement of certain diazoamido-bodies into amido-azoderivatives (p. 114).
- 6. By action of diazo-salts (a) upon tertiary anilines, and (b) upon m diamines.

The last two methods lead to amido-derivatives of the azo-hydrocarbons, some of which have become very important for the coal-tar color industry.

Mixed azo-derivatives are frequently obtained by combining diazosalts with suitable fatty bodies—i. e., such as contain easily replaceable hydrogen atoms in union with carbon, or with heterocyclic compounds like pyrrol, pyrazole, etc.

Properties.—The azo-bodies are more intensely colored than the paleyellow azoxy-derivatives. They do not unite with acids, if they do not contain an additional basic amido-group. They can be directly chlorinated, nitrated, and sulphonated. Reducing agents convert them into hydrazo-compounds (p. 116), or decompose them at the point of double union with the production of amido-compounds. The latter reaction serves to determine the constitution of the amidoazo-derivatives.

Symmetrical Azo-compounds.—Azobenzene, Indifferent, Azobenside, C.H. N = NC.H., melting at 68° and boiling at 293°, was discovered by Mitscherlich in 1834. It forms orange-red, rhombic crystals, readily soluble in alcohol and ether, but sparingly soluble in It is produced by the methods outlined above from nitrobenzene, aniline, and hydrazobenzene. Azoxybenzene yields it on distillation with iron filings (B. 207, 329). It has also been obtained from potassium aniline by action of air, and from aniline and sodium (B. 10, 1802). It is converted into benzidine by tin and hydrochloric acid; this is due to a transposition of the hydrazobenzene first formed.

o-Nitroasobenzene melts at 127° (B. 19, 2157; R. 441). p-Nitroasobenzene melts at 137°. sym.-m-Dinitroasobenzene is an oil (B. 18, R. 627). p-Dinitroasobenzene melts at 206°. Dinitrobenzene-azobenzene melts at 117° (B. 21, R. 400; 22, R. 744).

Azotoluenes.—o-Azotoluene melts at 157°. m-Azotoluene melts at 55°. p-Azotolu-

ene melts at 143° (B. 17, 463; 18, 2551). Azoxylenes and azotrimethyl benzenes are

Mixed Azo-compounds.—Benzene-azomethane, azophenylmethane, CaHaN = NC- H_3 , boiling at about 150°, and Bensene-assethane, C_4H_5 . $N=NCH_2$. CH_3 , boiling at about 180°, are liquids with a peculiar odor. They are obtained by oxidizing the corresponding hydrazines with mercuric oxide. Sulphuric acid transposes benzene-azoethane into the isomeric acetaldehyde-phenylhydrazine, C₄H₅NH . N: CH . CH₃ (B. 29, 794). Bensene aso-nitroethane, C₈H₅N = NCH(NO₂). CH₂, melting at 137°, formed from diazobenzene nitrate and sodium nitroethane, consists of orange-colored laminse, and forms salts with two equivalents of alkali (B. 8, 1076; 9, 384).

Other compounds which can be regarded as mixed azo-derivatives are the benzenedies. carboxylic acids and their derivatives, the diazocyanides (p. 103), diphenylsulphocarbazone and carbdiazone (p. 128), the formasyl compounds (p. 129), bensoyl-diazobenzene (see this), as well as numerous azo-bodies resulting from the combination of diazo-salts with suitable heterocyclic derivatives—e. g., pyrrol, pyrazole, etc.

Amidoazo-compounds. — The indifferent azo-derivatives are all orange-yellow to orange-red in color, but they are not dyes. By the introduction of a salt-forming group the resulting bodies, like amido-azocompounds, oxyazo-compounds, and especially amidoazobenzene sulphonic acids, do become colors applicable in the dyeing of wool and silk. The number of azo-dyes is very great. Some of the simplest will be discussed in the following paragraphs, while the most important representatives of the class, technically speaking, will be considered in other portions of this book, particularly in connection with the naphthalene group. The sulphonic acids of the amidoazo-bodies are of greater importance than the parent substances.

Formation.—(1) From diazoamido-compounds: p-amidoazobenzene is obtained from diazoamidobenzene. In the case of diazoamidobenzene this transposition occurs on standing with alcohol, but more readily by

the action of a slight quantity of aniline hydrochloride.

This reaction only occurs readily if in the reacting diazoamido-compound the position in the benzene nucleus adjacent to the amido-group

in the para place be unoccupied.

However, compounds, like diazoamido-p-toluene, CH₃[4]C₄H₄[1]N $= N - NH[1']C_8H_1[4']CH_3$, in which the p-position with reference to the imido-group is occupied by CH_3 , also suffer this transposition. It occurs on heating diazoamido-p-toluene, dissolved in fused p-toluidine, to 65° with p-toluidine.

The amido-group of the resulting amido-azo-toluene occupies the o-position with reference to the diazo-group. It is o-amidoazotoluene or [4] Methyl-benzene-azo-[4']-methyl-[2']-amidobenzene, $CH_3[4]C_6H_4[1]N =$

 $N[1']C_6H_3[4']CH_3[2']NH_3(B.17,77).$

(2) By the action of the diazo-compounds (a) upon the tertiary aromatic amines, or (b) upon m-diamines in neutral or feebly acid solution (B. 10, 389, 654):

$$\begin{array}{ll} C_6H_5\,.\,N_2\,.\,NO_3 + C_6H_5N(CH_3)_3 &= C_9H_5\,.\,N = N\,.\,[1]C_9H_4[4]N(CH_3)_3 + NO_3H \\ C_6H_5\,.\,N_2\,.\,NO_3 + C_6H_4\left\{ \begin{bmatrix} 1\\3\end{bmatrix}NH_2 \\ \end{bmatrix} = C_6H_5\,.\,N = N\,.\,[1]C_9H_3\left\{ \begin{bmatrix} 2\\4\end{bmatrix}NH_3 \\ \end{bmatrix} + NO_3H. \end{array}$$

The first products with primary and secondary monamines, especially in neutral or acetic acid solution (B. 24, 2077), are diazoamido-compounds, which under the previously mentioned conditions are capable of rearranging themselves into amidoazo-derivatives.

The phenols act like the tertiary amines upon diazo-salts with the formation of oxyazo-derivatives, which will be discussed later after the

amidophenols.

Properties and Deportment.—The amido-azo-compounds are usually crystalline, and generally dissolve readily in alcohol. They are yellow, red, or brown in color. Their salts with acids are the valuable technical amido-azo-dyes. (1) Their decomposition upon reduction and the great importance of this reaction have been previously dwelt upon (p. 113) (B. 21, 3471). Occasionally, decomposition such as this takes place on heating the bodies with hydrochloric acid (B. 17, 395). (2) Amidoazo-compounds may be changed to diazo-azo-derivatives with nitrous acid. Isodihydrophen-tetrazines may be obtained by reducing the diazosalts of o-amido-azo-derivatives. (3) Indulines (see these) are produced on heating p-amido-azo-compounds with aniline hydrochloride, and eurhodines when o-amido-azo-bodies are employed. (4) When the o-amidoazo-compounds are oxidized they become pseudoazimido-derivatives. (5) The o-amido-azo-compounds combine with aldehydes. Condensation products result, which are derived from dihydrophentriazine (see this).

Many chemists consider the o-amido-azo-compounds to be quinon-imides: $C_6H_5NHN = C_6H_4 = NH$ or $C_6H_5NHN - C_6H_4 - NH$ (B. 23, 497); compare o-azophenols.

p-Amido-azobenzene, C₆H₅—N=N[1]C₆H₄[4]NH₄, consists of yellow leaflets or needles, melting at 123° and boiling undecomposed above 360°, but at 225° under 12 mm. It can be obtained from p-nitro-azobenzene (p. 113), and is made technically by the rearrangement of diazoamidobenzene (p. 109) (B. 19, 1953; 21, 1633), which does not need to be isolated for this purpose. Manganese dioxide and sulphuric acid oxidize it to quinone. It breaks down into aniline and p-phenylene-diamine upon reduction (p. 95). Its hydrochloride forms steel blue needles and, like the oxalate, has been applied as a yellow dye. It is prepared in the coal-tar industry upon a large scale, and serves as the starting-out material for the manufacture of disazo-dyes and indulines. Although the salts of amidoazobenzene have not any importance as dyes, yet the sulphonic acids, acid yellow or pure yellow (p. 138), possess more valuable and desirable dyeing properties. p-Acetamido-azo-benzene melts at 143°.

m-Amidoazobenzene, C₈H₅N₅[1]C₆H₄[3]NH₂, melts at 57°; its acet-derivative, melting at 131°, has been obtained from nitrosobenzene and acet-m-phenylene-diamine (B. 28, R. 982).

Benzene-azo-p-dimethylaniline, $C_eH_eN=N[1]C_eH_4[4]N(CH_s)_s$, melts at 116°. Bensene-azo-diphenylamine, p-phenylamido- or p-anilido-azobenzene, melts at 82°. o-Amidoazotoluene, $CH_s[2]C_eH_4[1]N=N[1']C_eH_3-\{[3']CH_s$, melting at 100°, is obtained from o-toluidine. m-Amidoazo-toluene, $CH_s[3]C_eH_4[1]N=N[1']C_eH_3-\{[2']CH_s$, melts at 80°. m-Nitrobenzene-azo-p-amidobenzene melts at 213° (B. 29, R. 661).

2,4-Diamido-azo-benzene, C₆H₅. N₂. C₆H₁(NH₂)₃, is produced by the action of diazobenzene-nitrate upon meta-phenylenediamine, and consists of yellow needles melting at 117°. Its hydrochloric acid salt

occurs in trade under the name chrysoidine, and dyes orange-red. Reduction changes it to aniline and unsymmetrical triamido-benzene, Cally (NH₂)₃ (p. 97).

Symmetrical p-Diamido-azo benzene, H₂N. C₃H₄. N₂. C₆H₄. NH₂, has been prepared by reducing nitroacetanilide, NO₂. C₆H₄. NH. C₂H₄O, with zinc dust and alkali; also, from diazo-phenylenediamine, etc. (B. 18, 1145), and by the reduction of p-dinitroazobenzene (see above) (B. 18, R. 628). It crystallizes from alcohol in yellow needles, melting at 241°.

Its tetra-alkylic derivatives are the so-called Azylines. They are formed when nitric

oxide acts upon the tertiary anilines (B. 16, 2768):

and in the action of the diazo-compounds of dimethyl-p-phenylenediamine (p. 95) upon tertiary anilines (B. 18, 1143):

$$(CH_3)_2N \cdot C_6H_4 \cdot N_2Cl + C_8H_5N(CH_3)_2 = (CH_3)_2N \cdot C_6H_4 \cdot N_2 \cdot C_8H_4N(CH_2)_2 + HCL$$

The azylines are red, basic dyes, which dissolve in hydrochloric acid with a purplered and in acetic acid with an emerald-green color. By reduction (stannous chloride, tin, and hydrochloric acid) they yield two molecules of dialkylic p-phenylenediamine. They are decomposed when heated to 100° with alkyl iodides (4 molecules); the products in this case are tetra-alkylic para-phenylenediamines.

Triamido-azo-benzene, $C_{12}H_{13}N_{5} = H_{2}N \cdot C_{5}H_{4} \cdot N_{2} \cdot C_{5}H_{3} < N_{1}H_{2}^{2}$, is formed when nitrous acid acts upon metaphenylene-diamine. At first, by transformation of an amido-group, we obtain a diazo-compound, which further reacts on a second molecule of the diamine. It forms salts with one, two, and three equivalents of the acids; of these the diacid are the most stable, while water decomposes the triacid. Its hydrochloric acid salt, mixed with Tetraamidophenylene-bis azobenzene, CaH4[N2C4 H₃(NH₂)₂]₂, is commercial Phenylene Brown (Manchester-brown, Bismarck-brown), which is applied in dyeing cotton and coloring leather.

15. HYDRAZINE COMPOUNDS.

The simplest aromatic hydrazine derivatives are: Phenylhydrasine, C₆H₅. NH. NH₂; unsym.-Diphenylhydrazine, (C₆H₆)₂N. NH₂, and sym.-

Diphenylhydrazine, CoH5NH. NH. CoH5, or hydrazobenzene.

Phenylhydrazine and unsym.-diphenylhydrazine both contain an NH,-They show similar reactions in many respects, whereas the symmetrical diphenylhydrazine deports itself rather peculiarly. following paragraphs sym.-diphenylhydrazine and its homologues, the hydrazo-compounds, the hydrazine derivatives longest known, will be placed at the head of the aromatic hydrazines. The hydrazo-compounds arrange themselves with the previously discussed azo-bodies, with which they possess many intimate connections. Then will follow the monophenyl- and the unsym.-diphenylhydrazine group.

Hydrazo-compounds.—Symmetrical diphenylhydrazine was discovered in 1863 by A. W. Hofmann upon reducing azobenzene with care, and inasmuch as it differed from the last compound in containing two hydrogen atoms more, it was called hydrazobenzene, a name which

has adhered to symmetrical diphenylhydrazine.

Formation.—Azobenzene and allied compounds yield hydrazobenzene upon reducing them with alcoholic ammonium sulphide, with zinc dust, and with potassium or sodium amalgam. It is not necessary to isolate the azo-body; the proper nitro- and azoxy-derivatives can be treated with zinc dust and sodium hydroxide. Nitro-compounds can also be converted in alkaline solution into hydrazo-derivatives by electrolytic reduction (Ch. Ztg. 17, 129, 209).

Hydrazo-benzene, sym.-Diphenylhydrazine, C₄H₅. NH. NH. C₄H₅, melting at 131°, decomposes at higher temperatures into azo-benzene and It is readily soluble in alcohol and ether, and crystallizes in colorless plates or leaflets, insoluble in water. It has an odor resembling that of camphor. When its alcoholic solution is exposed to the air, it

oxidizes to azo-benzene.

It is an indifferent body, and does not form salts with acids, but concentrated mineral acids occasion in it an interesting transposition. below, benzidine and semidine rearrangement.

Powerful reducing agents decompose hydrazobenzene into two mole-

cules of aniline.

Hydrazobenzene yields urea-derivatives with phenylisocyanate (B. 23, 490) and with phenyl mustard oil (B. 25, 3115); with benzaldehyde it forms diphenylhydrazibenzylene or benzhydrazofn, C₆H₆CH<N C₆H₆, melting at 55° (B. 19, 2239).

Monacetyl-hydrasobenzene melts at 159°. Diacetyl-hydrasobenzene melts at 105° (B. 17, 379; A. 207, 327).

o-, m-, and p-Methyl-hydrazobenzene or sym. o-, m-, and p-Tolylphenylhydrazine melt at 101°, 60°, and 86°.

sym.-Hydrazotoluenes, CH₃. C₄H₄. NH. NH. C₄H₄. CH₃. The ortho-compound melts at 165°; the meta is liquid (A. 207, 116), and the para melts at 124° (B. 9, 829).

Hydrazoxylenes (B. 21, 3141). sym. -Dihalogen hydrazobenzenes have been obtained from the corresponding azo-bodies. p-Diamidohydrazobenzene, diphenine, NH₂[4]C₆H₄[1]NH.NH[1']C₆H₄[4']-NH2, melting at 145°, results from the action of ammonium sulphide upon para-dinitroazo-benzene (B. 18, 1136).

Unsymmetrical nitrohydrasobenzenes have been obtained from chlordinitro- and chlortrinitrobenzene by the action of phenylhydrazine (A. 190, 132; 253, 2; J. p. Ch. [2]

37, 345; 44, 67). Compare further asymmetrical polynitrodiphenylamines (p. 93). Tetraphenylhydrazine, (C₄H₆)₂N — N(C₄H₆)₂, melting at 147°, results from the action of iodine upon diphenylamine sodium, (C₄H₆)₂NNa (B. 29, R. 87).

THE BENZIDINE AND SEMIDINE REARRANGEMENT OR TRANSPOSITION OF THE HYDRAZO-COMPOUNDS.

Hydrazobenzene sustains a very remarkable rearrangement into an isomeric compound when it is treated with acids. When azobenzene is reduced in acid solution, the hydrazobenzene which is produced does not form salts, but even in the cold is changed by mere contact with acids into a diamine, a diacid base: benzidine (see this) or p-diamidodiphenyl. Benzidine, a starting-out substance for the preparation of substantive cotton dyes, is prepared technically in the wet way. Diphenyline (see this), o,p-diamido-diphenyl (B. 17, 1181), occurs in small quantities, together with benzidine:

The chief or principal rearrangement, in which the two amido-groups arrange themselves in the para-position with reference to the point of union of the two benzene nuclei, is known as the *benzidine-rearrangement* of the hydrazo-compounds.

Mineral acids convert sym.-o- and m-ditolyl hydrazine or o- and m-hydrazotoluene and other hydrazo-compounds, in which the p-hydrogen atoms referred to the imidogroups in both aromatic residues are free, into the corresponding p-diamido ditolyls or tolidines.

If, however, p-hydrazotoluene be treated with aqueous mineral acids, it changes in part to p-azotoluene and p-toluidine, and partly to o-amidoditolylamine (B. 27, 2700). The latter body is principally formed by the action of stannous chloride and hydrochloric acid upon hydrazotoluene:

$$CH_3 \frac{H}{H} \frac{H}{H} HN - NH \frac{H}{H} \frac{H}{H} CH_3 \longrightarrow CH_3 \frac{H}{H} \frac{H}{H} NH \frac{H}{NH_2} \frac{H}{H} CH_3$$
p-Hydrazotoluene o-Amido-[4,3']-ditolylamine.

Hydrazo benzene itself, when acted upon in benzene with hydrochloric acid gas, yields small amounts of o-amidodiphenylamine (Ch. Ztg. 18, 1095):

$$H \xrightarrow{H H} NH = NH \xrightarrow{H H} H \xrightarrow{H H} H \xrightarrow{H H} NH \xrightarrow{H H} H.$$

This is the semidine rearrangement; it is so called because only the one NH-group is converted into an NH₂-group, and not both NH-groups, as in the bensidine rearrangement. In simple p-substituted hydrazobenzenes the amido-group can enter the o-or p-position with reference to the imido-group. Hence it is necessary to distinguish between an o- and p-semidine transposition.

Acetamidohydrazobenzene, melting at 146°, is changed by stannous chloride and hydrochloric acid into monacet-p-diamidodiphenylamine (B. 26, 704):

$$C_3H_3ONH\frac{H}{H}\frac{H}{H}NH-NH\frac{H}{H}\frac{H}{H}H \longrightarrow C_3H_3ONH\frac{H}{H}\frac{H}{H}NH\frac{H}{H}NH_3$$

Attention may here be directed to such transpositions in which anilines substituted at the nitrogen are converted, by the migration of the substituents, into anilines substituted in the nucleus. Usually, in these changes, compounds with feebly pronounced or neutral character yield more basic bodies. They are:

(1) The rearrangement of the phenylnitrosamines into p-nitroso-anilines (p. 97);
(2) that of the phenylnitramines (diazobenzene acids, p. 98) into p-nitranilines; (3) the β-phenylhydroxylamines (p. 70) into p-amidophenols; (4) the phenylhydrazines into p-phenylene-diamines (p. 120); (5) the chlorylanilines into p-chloranilines (see p-chloraniline, p. 92, and μ-methyltolimidazole; (6) the diazoamido- into p-amidoazo-bodies (p. 110); (7) the hydrazobenzenes into benzidines and amidodiphenylamines:

1

Those instances in which carbon groups wander from nitrogen to the nucleus—e. g., the rearrangement of the phenyl alkylamines into homologous anilines (p. 78), etc.—might also be included here. Compare also the transpositions of phenylsulphuric acid and phenylcarbonic acid into phenolsulphonic acid and salicylic acid (p. 147).

Phenylhydrazine Group.—Phenylhydrazine and unsym.-diphenylhydrazine are formed in the reduction of diazobenzene salts and diphenylnitrosamine, as well as from the reaction products produced when nitrous acid acts upon primary and secondary anilines:

Formation.—1. By the reduction of diazo-salts: (a) By the action of acid alkaline sulphites upon the diazo-derivatives. On allowing neutral potassium sulphite to act upon the yellow-colored potassium salt of diazobenzene sulphonic acid, when colorless potassium benzene hydrazine-sulphonate will be formed immediately:

$$C_aH_a - N = N - SO_aK + SO_aHK + H_aO = C_aH_aNH$$
. NHSO_aK + SO_aKH.

When the sulphonate is heated with hydrochloric acid, phenylhydrazine hydrochloride is produced, together with primary potassium sulphate:

$$C_6H_6.N_2.H_2.SO_2K + HCl + H_2O = C_6H_6.N_2H_2.HCl + SO_4KH.$$

The sulphazides—e.g., C₆H₅. NH. NH. SO₂. C₆H₅, phenyl-benzene sulphazide—are prepared by the action of free sulphurous acid upon the acid solution of diazobenzene salts.

p-Nitrodiazobenzene nitrate and two molecules of potassium sulphite yield potassium p-nitrophenylhydrazine disulphonate, $C_6H_4(NO_2)N(SO_2K)NH(SO_2K)$, which hydrochloric acid decomposes quantitatively into p-nitrophenylhydrazine.

In the same manner dipotassium sulphite changes potassium benzene diazosulphonate into potassium phenylhydrazine disulphonate, C₆H₅N-(SO₂K), Which can be more easily obtained from nitrosoacetanilide and dipotassium sulphite (p. 98). It is resolved by hydrochloric acid into phenylhydrazine and sulphuric acid, and decomposed by alkali into potassium benzene diazosulphonate (B. 30, 374).

- (b) Potassium diazobenzene sulphonate can be reduced with acetic acid and zinc dust.
- (c) By the action of stannous chloride and hydrochloric acid upon the diazo-chlorides (B. 16, 2976; 17, 572):

$$C_6H_6$$
. $N_2Cl + 2SnCl_2 + 4HCl = C_6H_6$. N_2H_8 . $HCl + 2SnCl_4$.

Diazobenzene alkali salts (p. 102), when reduced with sodium amalgam furnish a good yield of phenylhydrazine (B. 30, 339).

2. By the reduction of diazo-amido-compounds in alcoholic solution with zinc dust and acetic acid, when they decompose into anilines and hydrazines:

$$\begin{array}{l} C_6H_5\,.\,N_2\,.\,NH\,.\,C_6H_5\,+\,2H_2 = C_6H_5\,.\,N_2H_3\,+\,NH_2\,.\,C_6H_5\\ \text{Diazo-amido-benzene} & \text{Phenylhydrazine} & \text{Aniline.} \end{array}$$

3. By the reduction of the nitroso-amines (pp. 97 and 120) with zinc dust and acetic

acid, unsym.-alkylphenyl- or diphenyl-hydrazines are then formed, and the aliphatic hydrazines are obtained in a similar manner (1, 171):

Historical.—A. Strecker and Römer, in 1871, obtained potassium phenylhydrazine sulphonate by the interaction of diazobenzene nitrate and acid potassium sulphite, and when the same reagent was allowed to act upon the diazide of sulphanilic acid (p. 137) they got a soluble potassium salt, which, boiled with hydrochloric acid, yielded crystalline phenylhydrazine-p-sulphonic acid, C_0H_4 $\left\{ \begin{bmatrix} 1\\4 \end{bmatrix} NH.NH_2$, the first primary aromatic hydrazine compound, which must be viewed as a cyclic ammonium salt: C_0H_4 $\left\{ \begin{bmatrix} 1\\4 \end{bmatrix} NH-NH_1 \\ A \end{bmatrix} SO_2$. Emil Fischer, in 1875, demonstrated that potassium phenylhydrazine sulphonate was converted, on boiling with hydrochloric acid, into phenylhydrazine hydrochloride, from which sodium hydroxide liberated phenylhydrazine, an exceedingly reactive substance (B. 8, 589).

Properties.—The aromatic hydrazines are monacid bases, dissolving with difficulty in water, but easily in alcohol and in ether. At the ordinary pressure they boil with slight decomposition and without decomposition under diminished pressure. In the air they oxidize very readily, taking on a brown color. They reduce Fehling's solution.

Phenylhydrazine, C₆H₆NH — NH₂, forms plate-like crystals melting at 23°. It boils under 760 mm. at 241–242° with slight decomposition, and under 12 mm. pressure at 120° without decomposition. Its specific gravity at 21° equals 1.091. It is made, as already described under general methods of formation, by the reduction of diazobenzene chloride. Its transpositions are given below. It has, as a generator of antipyrine, met with wide application. It serves as an important reagent for the detection of aldehydes and ketones. The latter observation has become of particular importance in the development of the chemistry of the carbohydrates.

Its hydrochloride, C₆H₅NH. NH₂. HCl, consists of brilliant, white leaflets, dissolving with difficulty in concentrated hydrochloric acid. When it is heated to 200° with hydrochloric acid it yields p-phenylenediamine. For its salts with carboxylic acids consult B. 27, 1521.

Metallic sodium dissolves in phenylhydrazine, forming the sodium derivative, CaIIs.

NNa. NH_a. This is a yellowish red, amorphous mass.

Alkyls and acid residues can replace the sodium, thus producing a-phenylhydrazine derivatives (p. 127) (B. 19, 2448; 22, R. 604). Potassium phenylhydrazine (B. 20, 47).

Substituted Phenylhydrazines (A. 248, 94; B. 22, 2801, 2809).—p-Chlorphenylhydrazine melts at 83°. p-Bromphenylhydrazine melts at 106°. p-Iodphenylhydrazine melts at 103°. o-Nitrophenylhydrazine forms brilliant red needles, melting at 90° (B. 27, 2549).

o-Nitro-s-formylphenylhydrazide melts at 177° (B. 22, 2804). For the formation of hetero-rings from these nitro-bodies, see p. 122. p-Nitrophenylhydrazine melts at 157°

(B. 29, 1831).

Homologous Phenylhydrazines.—o. Tolyl-hydrazine melts at 59°. m. Tolyl-hydrazine is liquid. o. Tolyl-hydrazine melts at 61°. Pseudocumyl-hydrazine (A. 212, 338; B. 18, 91, 3175; 22, 834).

Unsymmetrical diphenylhydrazine, (CaHa)2N. NH2, melting at 34° and boiling at

220° (50 mm.), is made by reducing diphenyl nitrosamine (p. 98). It forms sparingly soluble diphenylhydrazones with glucoses. Ferric chloride oxidizes it to tetraphenyltetrazone (p. 131).

Behavior of the Phenylhydrazines.—(1) While the phenylhydrazines are pretty stable toward reducing agents, they may be readily reconverted into diazo-compounds by moderated oxidation; this is effected by the

action of mercuric oxide upon their sulphates or sulphonates.

When boiled with copper sulphate or ferric chloride, the phenylhydrazines throw off nitrogen and become benzenes—this reaction will also serve for the replacement of the diazo-group by hydrogen and by the halogens if the free phenylhydrazine be replaced by chlorine, bromine, or iodine (B. 18, 90, 786; 25, 1074). The liberated nitrogen also answers for the quantitative estimation of the hydrazines.

The phenylhydrazines also reduce Fehling's solution (B. 26, R. 234). Consult B. 28, R. 996; 29, R. 977, for additional reduction reactions

with phenylhydrazine.

(2) Sodium liberates hydrogen, and a-sodium phenylhydrazines result.

(3) Nitrous acid converts the phenylhydrazines into nitrosohydrazines (p. 131).

(4) The alkylogens replace imido- and amido-hydrogen in the phenyl-

hydrazines, finally forming phenylhydrazonium compounds.

(5) The aldehydes and ketones combine with the phenylhydrazines, usually with the immediate separation of water and formation of phenyl-This reaction, like the oxime formation, is characteristic of hvdrazones. the aldehydes and ketones.

(6) Acid radicals can also be readily introduced into the phenylhydra-

zines.

(7) When the phenylhydrazines are heated to 200° with fuming hydrochloric acid, they are transposed into paraphenylenediamines (see p. 118, and B. 28, 1538)

Phenylalkyl Hydrazines.—The a-derivatives are termed symmetrical, the β -compounds unsymmetrical alkylphenylhydrazines. Formation: (1) Both isomerides are produced by the action of alkyl bromides upon phenylhydrazine (A. 199, 325; B. 17, 2844). (2) The β -class is also obtained by the reduction of the corresponding mixed azo-bodies (p. 112). (3) The a-derivatives are obtained by the action of ethyl bromide upon sodium phenylhydrazine (B. 19, 2450, 22, R. 664; (4) by reduction of the corresponding nitrosamines (p. 97) with zinc dust; (5) by treating β acetphenylhydrazine, C_6H_6NH . NH. CO. CH₂, with halogen compounds, and saponifying with boiling, dilute acids (B. 26, 946).

a-Methyl-phenylhydrazine, C₆H₅. N(CH)₃. NH₂, melting at 131°(35 mm.), rearranges

itself to methyl-p-phenylenediamine.

a-Ethyl-phenyl hydrasine, C6H5. NH. NH(C2H5), boils at 231°. Both compounds are oxidized to tetrazones (p 131).

The a-ethyl compound unites with ethyl bromide to form CaH5. N(C2H5)2Br. NH2,

which by reduction yields diethyl-aniline.

a-Ethylene Phenylhydrazine, C₆H₅N < NH₂ NH₂ N . C₆H₅, melts at 90° (B. 21,

3203).

β-Methyl-phenyl hydrasine and β-Ethyl-phenyl hydrasine are colorless oils, oxidizing on exposure to air to benzene-azo-methane and ethane (p. 113), from which they can be obtained by reduction. The β -body can also be produced from antipyrine by boiling it with alcoholic potash (B. 25, 771).

β-Allyl-phenyl hydrazine boils at 177° (110 mm.) (B. 22, 2233). The di- and tri-alkylic phenylhydrazines are formed by letting alkyl iodides act won the sodium derivative of a-methyl-phenyl-formyl hydrasine, CaHaN(CHa)NNa. CH0, and then splitting off the formyl group with fuming hydrochloric acid.

and then spitting out the formyl group with ruming hydrochioric acid.

Dialkylic phenylhydrazines, by the action of alkyl iodides, are converted into quaternary azonium derivatives—e. g., C₆H₆N(CH₃)₂I. NH. CH₂—together with trialkyl phenylhydrazines. aβ-Dimethyl-phenyl hydrazine, C₆H₆N(CH₃)NH. CH₃, boils at 93° (7 mm.); phenyl-trimethyl hydrazine boils at 93° (8 mm.) (B. 27, 696). unsym.-Amido-phenyl-methyl hydrazine, NH₂[2]C₆H₆[1]N(CH₃)NH₂, is an oil which rapidly changes to a resin. It is produced upon reducing o-nitronitrosomethylaniline with alcoholic ammonium sulphide.

Hetero-ring Formations from o-substitution derivatives of phenylhydrazine. Azimidol results on boiling o-nitrophenylhydrazine with caustic alkali. a-Phentriazine is produced by reducing the formyl derivative of o-nitrophenylhydrazine with sodium amalgam and acetic acid. unsym.-o-Amido-phenyl-methyl hydrazine is converted by nitrous acid into

phen-methyldihydrotetrasine:

Phenylhydrazones.—Just as the aldehydes and ketones form oximes with hydroxylamine, so they combine to phenylhydrazones with phenylhydrazine. The compounds derived from the aldehydes are termed aldehydrazones (A. 247, 194 Anm.), and those from the ketones are the ketohydrazones, while the dihydrazones of the a-dicarbonyl-derivatives are the osazones (B. 21, 984):

$$R'$$
. CHO + NH, NHC₆H₅ = R' . CH = N. NH. C₆H₅ + H₂O (R')₂CO + NH₂. NHC₆H₅ = (R')₂C = N. NH. C₆H₅ + H₂O.

The osazone formation has become very important for the chemistry of the sugars (see 1, 546).

The phenylhydrazone formation is usually supposed to consist first in the production of an addition product, corresponding in its constitution to aldehyde ammonia. In a few instances-e.g., with oxaloacetic ester and dioxosuccinic ester-it has been possible to isolate the addition products, which split off water with ease and pass into phenylhydrazones:

$$\begin{array}{l} \text{CO}_{2}.\text{ C}_{2}\text{H}_{5}.\text{ CO} \\ \text{CO}_{3}.\text{ C}_{2}\text{H}_{5}.\text{ CO} \\ \text{CO}_{3}.\text{ C}_{2}\text{H}_{5}.\text{ CO} \\ \text{CO}_{3}.\text{ C}_{2}\text{H}_{5}.\text{ CO} \\ \end{array} \\ + 2\text{NH}_{2}.\text{ NH}.\text{ C}_{6}\text{H}_{5} = \frac{\text{CO}_{2}.\text{ C}_{2}\text{H}_{5}.\text{ C}}{\text{CO}_{3}.\text{ C}_{2}\text{H}_{5}.\text{ C}} < \frac{\text{NH}.\text{ NH}.\text{ C}_{6}\text{H}_{5}}{\text{CO}_{4}.\text{ NH}.\text{ NH}.\text{ C}_{6}\text{H}_{5}} \\ \text{CO}_{3}.\text{ C}_{2}\text{H}_{5}.\text{ C} < \frac{\text{NH}.\text{ NH}.\text{ C}_{6}\text{H}_{5}}{\text{CO}_{4}.\text{ NH}.\text{ NH}.\text{ C}_{6}\text{H}_{5}} \end{array}$$

That dioxosuccinic ester yields an addition product argues for the aldehyde-ammonia constitution, and against the view possible with oxaloacetic ester, that it is an ammonium salt corresponding to the formula CO₂. C₂H₅. CO. CH(NH₂. NHC₂H₅). CO₂C₂H₅ (A. **295**, 339).

As the phenylhydrazones are characteristic for bodies containing the aldehyde and ketone groups, it was but natural that they should have been frequently mentioned in connection with the aliphatic derivatives, and will also be again met with later in connection with the aromatic compounds in which aldehyde and ketone groups are present. It seems, however, advisable to refer briefly to the aliphatic phenylhydrazone derivatives. The following have received mention in the first volume of this work: Phenylhydrazones of the simple aldehydes; of the simple ketones; of the diketones; of glyoxylic acid; of pyroracemic acid; of acetoacetic ester; of lævulinic acid; of mesoxal-aldehyde; of acetone oxalic ester; of mesoxalic acid; of oxalacetic ester; of acetone dicarboxylic ester; of acetone diacetic acid; of tetroses; of oxalyldiacetone; of dioxosuccinic acid; of oxalosuccinic ester; of arabinose; of rhamnose; of the glucoses; of milk sugar; of maltose and isomaltose.

Formation of the Phenythydrazones.—(1) By the action of phenylhydrazine and unsym.-alkylphenyl or unsym.-diphenyl-hydrazine upon aldehydes and ketones (see above). (2) By the addition of phenylhydrazine to trebly linked carbon atoms; the phenylhydrazone of oxalo-acetic ester is also produced by the addition of phenylhydrazine to acetylene dicarboxylic ester:

$$\begin{array}{l} \text{CO}_{2}.\ \text{C}_{2}\text{H}_{5}.\ \text{C} \\ \text{CO}_{2}.\ \text{C}_{2}\text{H}_{5}.\ \text{C} \\ \end{array} + \text{NH}_{2}\text{NHC}_{6}\text{H}_{5} = \begin{array}{l} \text{CO}_{2}.\ \text{C}_{2}\text{H}_{5}.\ \text{C} = \text{N}.\ \text{NH}.\ \text{C}_{6}\text{H}_{5} \\ \text{CO}_{2}.\ \text{C}_{2}\text{H}_{5}.\ \text{CH}_{2} \end{array}$$

(3) By the interaction of diazobenzene salts and many aliphatic bodies, containing hydrogen atoms readily replaceable by alkali metals—e. g., malonic ester and acetoacetic ester in alkaline solution (potassium diazobenzene, p. 102):

$$\begin{aligned} &(\text{CO}_2\text{C}_2\text{H}_5)_2\text{CH}_2 + \text{C}_6\text{H}_5 - \text{N}_2\text{OH} = (\text{CO}_2\text{C}_2\text{H}_5)_3\text{C} = \text{N-NH} \cdot \text{C}_6\text{H}_5 + \text{H}_2\text{O} \\ &\text{Phenylhydrazone-mesoxaloester} \\ &\text{CO}_2\text{C}_2\text{H}_5\text{CH}_3 + \text{C}_6\text{H}_5 - \text{N}_2\text{OH} = \\ &\text{CO}_2\text{C}_2\text{H}_5\text{C} = \text{N-NHC}_6\text{H}_5 + \text{H}_2\text{O} \\ &\text{CH}_3 \cdot \text{CO} \\ &\text{Phenylhydrazone-acetoglyoxylic Ester.} \end{aligned}$$

The body obtained from diazobenzene and malonic ester is identical with that derived from mesoxalic ester and phenylhydrazine. The idea that these bodies are hydrazones has been proved, among other ways, in the following manner:

(I) Dilute caustic alkali saponifies the phenylhydrazone of acetoglyoxylic ester, and

breaks down the acid into carbon dioxide and pyroracemic aldehyde-hydrazone. (2) The latter compound, acted upon with chloracetic ester and sodium ethylate, yields an ester from which anilidoacetic acid is obtained by reduction. This could only be possible if the chloracetic acid residue was joined to the same N-atom, with which the phenyl group had been attached (A. 247, 190):

$$CO_3. C_2H_5. C = N. NHC_8H_5 \longrightarrow CH_3. CO. CH = N-NHC_8H_5$$

$$CH_3. CO. CH = N-N < C_9H_5$$

$$CH_3. CO_3. C_3H_5 \longrightarrow CO_3. HCH_2NH. C_8H_5$$

The tendency to phenylhydrazone formation is so great that diazobenzene chloride expels carbon dioxide from alkylacetoacetic esters and the acetyl group from alkylic acetoacetic esters, with the production of the phenylhydrazone of an a-diketone and phenylhydrazones of a-ketone carboxylic esters respectively:

$$\begin{array}{lll} CH_{3}\cdot CH\cdot CO_{2}H & + C_{6}H_{5}N_{2}CI & = & \\ CH_{3}\cdot CO & + C_{6}H_{5}N_{2}CI & = & \\ CH_{3}\cdot CH\cdot CO_{2}\cdot C_{2}H_{5} & + C_{6}H_{5}N_{2}CI + H_{2}O & = & \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CO & + C_{6}H_{5}N_{2}CI & + H_{2}O & = & \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CC\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CC\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CC\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CC\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CC\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CC\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CC\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CC\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CC\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CC\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}\cdot CC\cdot CO_{2}II + HCI \\ CH_{3}\cdot CC\cdot CO_{2}C_{2}H_{5} & + CH_{3}$$

Nitrous acid acts similarly with formation of oximes (vol. 1). (3) Phenylhydrazine converts the monoximes of a-aldehyde ketones and a-diketones into hydrazeximes: thus, methylglyoxaloxime yields methylglyoxalphenylhydrasoxime, CH_a . C = (N - NH-

Transpositions of the Phenylhydrasones.—The phenylhydrazones are resolved into their original components on digesting them with dilute mineral acids. By carefully moderated reduction many phenylhydrazones have been converted into phenylhydrazides (see phenylhydrazido-acetic acid, p. 126; B. 28, 1223); consult B. 30, 736, upon the oxidation of phenylhydrazones.

Very few classes of organic compounds are capable of entering into the formation of heterocyclic bodies to the extent manifested by the hydrazine derivatives, whose intramolecular condensation reactions are, therefore, of the utmost importance in the development of the chemistry of ring-systems containing nitrogen. Some of the most important condensations have been met in connection with the phenylhydrazones of the fatty compounds, and will be again given in condensed form, while others will receive mention at the conclusion of the acid hydrazides.

(1) Indols result upon heating the phenylhydrazones of aldehydes, ketones, and ketonic acids with zinc chloride, stannous chloride, or mineral acids.

(2) Osotetrazones are produced when the osazones or a-diphenylhydrazones of a-dialdehydes, a-aldehyde-ketones, and a-diketones are oxidized.

(3) Boiling acids change the a-osazones and osotetrazones to osotriasoles.

(4) Dehydrating agents convert a hydrazoximes into osotriasoles.

(5) Pyrazoles result from the phenylhydrazones of the 1,3-oxymethylene ketones and eta-diketones by the exit of water; they are ring-shaped, nitrogen derivatives of the 1,3-olefine ketones.

6) The phenylhydrazones of 1,4-diketones rearrange themselves into n-anilidopyrrols. In preparing ring-shaped condensation products of the hydrazones the latter have frequently not been isolated, but simply worked over.

The following scheme represents the hetero-ring-formations possible with the phenyl- $\begin{array}{c} \text{CH}_3.\text{C} &\longrightarrow & \text{CH}_3.\text{C} &\longrightarrow & \text{CH}_4.\text{C} &\longrightarrow & \text{C}_4\text{H}_4 &\longrightarrow & \text{C}_$

$$\begin{array}{c} \text{CH} = \text{N-NHC}_{6}\text{H}_{5} \\ \text{CH} = \text{N-NHC}_{6}\text{H}_{5} \\ \text{CH} = \text{N-NHC}_{6}\text{H}_{5} \\ \text{CH}_{3}.\text{C} = \text{N-NC}_{6}\text{H}_{6} \\ \text{CH}_{3}.\text{C} = \text{N-NH}_{6}\text{H}_{6} \\ \text{CH}_{3}.\text{C} = \text{N-NH}_{6}\text{H}_{6} \\ \text{CH}_{3}.\text{C} = \text{N-NH}_{6}\text{H}_{6} \\ \text{CH}_{3}.\text{C} = \text{N-NH}_{6}\text{H}_{6} \\ \text{CH}_{4}.\text{C} = \text{N-OH} \\ \end{array} \qquad \begin{array}{c} \text{CH}_{3}.\text{C} = \text{N} \\ \text{CH}_{3}.\text{C} = \text{N-NH}_{6}\text{H}_{6} \\ \text{CH}_{4}.\text{C} = \text{N-OH} \\ \end{array} \qquad \begin{array}{c} \text{Diaceto-osotriazone, or n-Phenyldimethyl-osotriazole} \\ \text{CH}_{4}.\text{C} = \text{N-OH} \\ \end{array}$$

a-Methyl Indol, or Methyl

Glyoxalosotetrazone

PHENYLHYDRAZINE DERIVATIVES OF INORGANIC ACIDS.

Thionyl Phenylhydrazone, C₈H₈NH. N = SO, melting at 105°, consists of sulphur-yellow colored prisms. It is obtained, like the *thionyl alkylamines* (1, p. 170) and *thionyl anilines* (p. 80), by the interaction of thionyl chloride and phenylhydrazone. All phenylhydrazines having a free amido-group yield thionyl phenylhydrazone is more easily produced when thionyl anilonyl anilonyl melting of the phenylhydrazone. Further, it results upon gently directing of the production with this control. hydrazine. Further, it results upon gently digesting phenylhydrazine sulphinic acid, CaHaNH. NH. SOOH, obtained from sulphur dioxide and phenylhydrazine (B. 23, 474). Thionyl chloride, acetyl chloride, and other acid chlorides rearrange thionyl phenylhydrazine into diasobensene chloride, in that it reacts as if it were diasobensene sulphoxide (p. 100), C₈H₈N = N. S(OH) (A. 270, 114).

Phenylhydrazine Sulphonic Acid, C₈H₈NH. NH. SO₈H.—The potassium salt

is formed in the reduction of potassium benzene-diazosulphonate with sulphurous acid or monalkali sulphites. Consult p. 120 for the behavior of the potassium salt toward mineral acids, and the rôle it plays in the history of the discovery of phenylhydrazine.

p-Nitrophenylhydrazine Disulphonic Acid, C₈H₄(NO₂)N(SO₃H)NH(SO₃H).-Its dipotassium salt consists of sulphur-yellow needles, formed on adding an excess of a sulphite solution to nitro-diazo benzene ester, nitrate, or isodiazobenzene potassium. Hydrochloric acid resolves it into p-nitrophenylhydrazine, and it dissolves in an excess

of potash to a red tripotassium salt, C₂H₄(NO₄)N(SO₂K)NK(SO₂K) (B. 29, 1830).

Phenylbenzene Sulphazide, C₂H₅NH. NH. SO₂C₂H₅, melts with decomposition at 148–150°. It is formed from phenylhydrazine and benzene sulphochloride in ethereal solution, as well as from a diazobenzene salt solution by the action of sulphur dioxide (p. 120) (B. 20, 1238). See A. 270, 123, for the action of PCl₃, POCl₃, PSCl₃, AsCl₃, BCl₃, SiCl₄ upon phenylhydrazine.

Carboxylic Acid Derivatives of Phenylhydrazine.—Acid residues of the most varied character can be as readily introduced into phenylhydrazine, and generally by the same methods, as into aniline. The domain of the bodies thus won from phenylhydrazine is scarcely less extensive than that of the acid derivatives of aniline, and in the multiplicity of phenomena really surpasses it.

The acid hydrazides and the hydrazido-acids have shown themselves to be as well adapted as the phenylhydrazones for the formation of heterocyclic derivatives. Each group of carboxylic derivatives of phenyl-hydrazine will be followed by the most important hetero-ring formations, arranged in tabular form, which will later be discussed in a different connection in the section devoted to "heterocyclic compounds."

The amidrasones and formazyl derivatives will receive attention at the conclusion of

the simpler carboxylic derivatives of phenylhydrazine.

Fatty Acid Derivatives.—The fatty acid residues enter the amido-group of phenylhydrazine very readily with the production of sym. or β -acidyl compounds. or a-acidyl-compounds are made (1) by the action of acid chlorides or anhydrides upon sodium phenylhydrazine (B. 22, R. 664); (2) by action of suitable haloid derivatives upon β acetylphenylhydrazine, and subsequent splitting-off of the β -acet-group on boiling with dilute sulphuric acid, when the group occupying the a-position will not be attacked (B. 26, 945).

The sym.-phenylhydrazides, treated with ferric chloride and concentrated sulphuric acid, yield reddish to bluish violet colors, whereas the unsym. bodies are not colored

(B. 27, 2965, Bülow's reaction).

sym.-Formylphenylhydrazide, CaH,NH. NH. CHO, from formic acid and phenylhydrazine, melts at 145° (B. 27, 1522; 28, R. 764).

unsym.- or a-Acetphenylhydrazide, CaH5N(COCH2)NH2, from ab-diacetphenyl-

hydrazine on heating with dilute sulphuric acid, melts at 124° (B. 27, 2964). sym. or β -Acetphenylhydrazide, C_qH_aNH . NH. CO. CH_a , melting at 128°, is obtained from phenylhydrazine with acetic anhydride, or upon boiling with glacial acetic acid (A. 190, 129). $a\beta$ -Diacetphenylhydrazide, $C_qH_aN(CO.CH_a)NH.CO.CH_a$, melting at 106°, results when acetyl chloride acts upon potassium phenylhydrazine in ethereal solution (B. 20, 47).

Hetero-ring Formations of the Fatty Acid Phenylhydraside Derivatives:

n. Phenyltriasole results when formylphenylhydrazide is heated with formamide (B. 27, R. 801). n. Diphenylisodihydrotetrazine is also a formic acid derivative of phenylhydrazine: It results from the action of chloroform and caustic potash upon phenylhydrazine (compare action of chloroform and caustic potash upon primary amines: 1, 236, and 11, 84, isonitriles or carbylamines).

The sym. or β -acidylphenylhydrazides, treated with phosgene, thiophosgene, and isocyanphenyl chloride, yield heterocyclic compounds—the oxybiasoline derivatives (B. 26,

2870), which can also be regarded as derivatives of carbonic acid:

$$\begin{array}{c} C_{e}H_{5}NH.NH.CHO & \xrightarrow{H.CONH_{9}} C_{e}H_{5}N & \xrightarrow{N} CH \\ CH=N & CH=N \\ \hline \\ C_{e}H_{5}.NH.NH_{2} & \xrightarrow{HCCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{N} C \\ \hline \\ C_{e}H_{5}NH.NH.CO.CH_{9} & \xrightarrow{CCl_{9}} C_{e}H_{5}N & \xrightarrow{CCl_{9$$

n-Phenyltriazole

n-Diphenylisodihydrotetrazine

n-Phenyl - c -methyloxybiazolon

n-Phenyl - c -methylthio-oxybiazoline

n-Phenyl - c -methylphenylimido - oxybiazoline.

Alcohol Acid Derivatives of Phenylhydrazine. - sym. - Phenylhydrazidoacetic Alcohol Acid Derivatives of Phenylhydrazine. — sym. -Phenylhydrazidoacetic acid, C₆H₆NII · NH · CH₂ · CO₂H, melts at 158°; see vol. 1, 360. unsym. -Phenylhydrazidoacetic acid, C₆H₅N(NH₂)CH₂· CO₂H, melting at 167°, is obtained by the careful saponification of its liquid ethyl ester, the reduction product from nitrosophenylglycin ester, C₆H₅N(NO) · CH₂ · CO₂ · C₂H₅ (B. 28, 1223); its phenylhydrazide, melting at 178°, is formed from chloracetamide and phenylhydrazine (B. 29, 622).

β-Phenylhydrazido-β-propionic Ester, C₆H₅N(NH₂)CH₂· CH₂· CO₂· C₂H₅, boiling at 175° (9 mm.), is obtained from nitroso-β-anilidopropionic ester (B. 29, 515).

β-Phenylhydrazido-β-butyric Acid, C₆H₅N(NH₂) · CH(CH₂)CH₂COOH, from β-chlorbutyric ester and phenylhydrazine, melts at 111° (J. pr. Ch. 45, 87).

Hetero-ring Formations of the Phenylhydrasido-acids.—(1) Unsymmetrical phenylhydrazido-acetic ester condenses with formamide to phenylketodihydro-a-triazine. (2)

n-Diphenylketodihydro-a-triazine (see below) is similarly obtained from unsym.-anilido-

acetic acid-a-phenylhydrazide, $C_6H_6N(NH_2)CO$. CH_2 . NHC_6H_6 .

The phenylhydrazido-carboxylic acids (3, 4, 5) corresponding to the β -oxyacids show such readiness to anhydride (pyrazolidone- or lactasam-) formation that frequently it is

impossible to isolate them:

1.
$$C_8H_5N \cdot NH_2$$
 $C_8H_5N - N = CH$ $CH_2 \cdot COOC_2H_5$ $CH_2 - CO - NH$ $CH_3 \cdot COOC_2H_5$ $CH_4 - CO - NH$ $COOH_4 \cdot COOH_5 \cdot CO - CH_3 - NC_6H_5$ $CO - CH_3$ $CO -$

3.
$$C_6H_8NHNH_2 = \left\{ \begin{array}{c} CICH_2.CH_2.CO_2H \\ \hline CH_2 = CH.CO_2H \\ \end{array} \right. \xrightarrow{C_6H_6N-NH} CO-CH_2-CH_2$$
1-Phenyl - 5- pyrazolidone

4.
$$C_6H_6NH.NH_2 + CH_2.CH:CH.CO_2H \rightarrow \begin{array}{c} C_6H_5N...NH \\ CO...CH_3.CH.CH_3 \\ CO...CH_3.CH.CH_4 \\ CH_3.CH...CH_4 \\ CO...CH_3.CH...CH_4 \\ CH_3.CH...CH_4 \\ CH_4.CH...CH_4 \\ CH_4.CH...CH_4 \\ CH_5.CH...CH_4 \\ CH_5.CH...CH_4 \\ CH_6.CH...CH_4 \\ CH_6.CH...CH_6 \\ CH_$$

Phenylhydrazine Derivatives of the Mono-ketonic Acids.—The a-, β -, and γ -ketone carboxylic esters react with phenylhydrazine, forming phenylhydrazones, just as the ketones do. The phenylhydrazones of a- and γ -ketone carboxylic acids are known. Zinc chloride or concentrated sulphuric acid rearranges the phenylhydrazones of the a-, β -, and γ -ketone carboxylic acids into indol derivatives (compare indol formation of the ketone phenylhydrazones, p. 124). The phenylhydrazones of the β - and γ -ketone carboxylic esters and of the free γ -ketone carboxylic esters manifest great tendency to the lactazam formation. Lavulinic-phenylhydrazone (1, 360) yields 1-phenyl-3-methylpyridazinone (see this), and under other conditions a-methylindol- β -acetic acid. Acetoacetic Ester Phenylhydrazone, $C_6H_8NH.N = C(CH_3).CH_4.CO_2C_2H_8$, melting at 50°, is formed on adding acetoacetic ester to phenylhydrazine (B. 27, R. 793), and spontaneously forms 1-phenyl-3-methylpyrazolon (see this); whereas with acetyl chloride or excessive hydrochloric acid it yields 1-phenyl-3-methyl-5-ethoxypyrazole (see this).

Hetero-ring Formations of the Phenylhydrazone-ketonic Acids.

I. Indol condensation (see p. 124):

$$\begin{array}{c} \text{CH}_3 \cdot \text{C} = \text{N-NHC}_6\text{H}_5 & \text{CH}_3 \cdot \text{C-NH} \\ \text{CH}_2 - \text{CH}_2 - \text{COOH} & \text{COOH} \cdot \text{CH}_2 \cdot \text{C} & \beta \text{-acetic Acid} \end{array}$$

2. Lactazam formation:

- I-Phenyl-3-methyl-5-pyrazolon
- I-Phenyl-3-methylpyridazinone

3. Pyrazole formation:

Phenylhydrazine Derivatives of Carbonic Acid.— Phenylhydrazine Phenylcarbazinate, C₆H₅NH. NH. COONH₂NHC₆H₅, is produced on saturating an aqueous emulsion of phenylhydrazine with earbonic acid. It is a white crystalline mass (B. 190, 123). Ethyl Phenylcarbazinate, C₆H₅NHNHCOOC₂H₅, melting at 86°, is produced when chlorcarbonic ester acts upon an ethereal phenylhydrazine solution. When it is heated to 240° it loses alcohol and becomes diphenylurazine (A. 263, 278; B. 26, R. 20). unsym.-Phenylhydrasido-formic Ester, C₆H₅N(NH₂)CO-OC₂H₅, is an oil, obtained from its acet-derivative, which results from the interaction of acetphenylhydrazine and chlorformic ester (B. 29, 829).

heated to 240° it loses alcohol and becomes diphenylurasine (A. 263, 278; B. 26, R. 20). unsym.-Phenylhydrasido-formic Ester, C₈H₆N(NH₂)CO-OC₂H₅, is an oil, obtained from its acet-derivative, which results from the interaction of acetphenyl-hydrazine and chlorformic ester (B. 29, 829).

Phenylsemicarbaside, C₈H₆NH. NH. CONH₂, melting at 172°, is obtained from phenylhydrazine salts and potassium cyanate (A. 190, 113), or upon heating phenylhydrazine with urea or urethane. When heated it becomes phenylurazole and diphenyl-urazine, with the formation of CO, CO₂, NH₂, and benzene (B. 21, 1224). Phenylsemicarbazide, like sym.-acetphenylhydrazine (p. 125), is transposed by COCl₂, CSCl₂, and C₈H₅NCCl₂ into oxybiasolon-derivatives (B. 26, 2870). It forms benzeneazocarbonamide when its nitroso-compound (D. 131) is oxidized.

when its nitreso-compound (p. 131) is oxidized.

Diphenylcarbaside, (C₆H₅. NH. NH)₂CO, melting at 151°, results upon heating arethane with phenylhydrazine (B. 20, 3372) (compare B. 29, R. 982). A dicarbox-

ethyldiphenylcarbaside, (C₆H₆NCO₂C₇H₆. NH)₂CO, melting at 19°, results from the action of COCl₂ upon unsym. phenylhydrazidoformic ester (B. 29, 829).

Cyclic Urea and Carbamic Acid Derivatives: Phenylurasole is produced on heating

phenylsemicarbazide, or phenylhydrazine hydrochloride with urea, or biuret with phenylhydrazine. Diphenyluracine results upon heating ethylphenylcarbazinate and phenyl-

semicarbazide (A. 263, 582).

1-Phenyl-3-methyl-5-triazolon is obtained from acetyl urethane and phenylhydrazine (B. 22, R. 737).

$$\begin{array}{c} C_6H_5NH.NH_2 + 2NH_2.CO.NH_2 \longrightarrow \begin{array}{c} C_6H_5N \longrightarrow CO \\ NH \longrightarrow CO \\ NH \longrightarrow CO \\ \end{array} \\ \begin{array}{c} 2C_6H_5NH.NH.CO.OC_3H_5 \longrightarrow C_6H_5N \longrightarrow NH \longrightarrow CO \\ 2C_6H_5NH.NH.CONH_2 \longrightarrow \begin{array}{c} CO \longrightarrow NH \longrightarrow NC_6H_5 \\ \end{array} \\ \begin{array}{c} C_6H_5N \longrightarrow CO \longrightarrow NH \longrightarrow CO \\ \end{array} \\ \begin{array}{c} C_6H_5NH.NH_2 + NH < \begin{array}{c} COOC_2H_5 \longrightarrow C_6H_5N \longrightarrow CO \\ \end{array} \\ \begin{array}{c} C_6H_5N \longrightarrow CO \longrightarrow NH \longrightarrow CO \\ \end{array} \\ \begin{array}{c} I \cdot Phenyl \cdot 3 \cdot methyl \cdot 5 \cdot triazolon. \end{array}$$

Phenylhydrazine Derivatives of Thiocarbonic Acid.—On mixing an ethereal solution of phenylhydrazine with carbon disulphide, Phenylhydrazine Phenylsulphocarbasinate, C₆H₅NH. NH. CSSNH₅NHC₆H₅, results. It melts at 96°. Mineral acids liberate the acid from solutions of salts of phenylsulpho-carbazinic acid. It separates in delicate, shining leaflets, which readily oxidize to the corresponding disulphide (A. 190, 114). When the potassium salt of the acid is treated with COCl₂, CS₂, and ethylene bromide, the products are: n-phenylthiobiazolorsulphydrate, n-phenyldithiobiazoline sulphydrate, and n-phenylthiobiazoline sulphydrate.

and n-phenylthiopentahydrodiasthine (B. 27, 2516).

Phenylsulphosemicarbazide, C₈H₅NH . NH . CSNH₂, melting at 200°, is obtained from phenylhydrazine rhodanate at 160-170°. When heated to 130° with hydrochloric acid, it becomes sulphocarbizine or benzodiazthine (see this) (B. 27, 871). Diphenylsulphosemicarbaside, C₈H₅NH . NH . CS . NHC₈H₅, from diphenylcarbazinic acid and aniline (B. 29, 1686), is converted by nitrous acid into diphenylisotetrasolom

Diphenylsulphocarbazide, (CaH5NH. NH)2CS, melting at 150°, is formed when

phenylhydrazine phenylsulphocarbazinate is heated to 100-110°.

Diphenylsulphocarbazone, C₆H₅N = N. CSNH. NH. C₆H₅, consists of bluish-black crystals, and is formed by brief boiling of diphenylsulphocarbazide with moderately concentrated alcoholic potash. Diphenylsulphocarbodiazone, $(C_6H_5N=N)_2CS$, from diphenylsulphocarbazone by

oxidation with hydrated manganese peroxide, consists of red needles (A. 212, 316).

Hetero-ring Formations of the Phenylhydrasine Thiocarbonic Acid Derivatives:

$$C_{6}H_{5}NH . NH . CSSK$$

$$C_{6}H_{5}NH . NH . CSSH_{2}$$

$$C_{7}H_{1}$$

$$C_{8}H_{1}NH . NH . CSSH_{2}$$

$$C_{8}H_{1}NH . CSSH_{2}$$

$$C_{8}H_{1}NH$$

Phenylhydrazine Derivatives of Guanidine. - Anil Guanidine, NH: C(NH2). NHNHCaHs, and Amidophenyl guanidine, NH: C(NH2). N(CaH3)NH2, are formed together from cyanamide and phenylhydrazine (B. 29, R. 1109); under other conditions the product is a phenylhydrazine derivative of biguanide—the easily decomposable Anilbiguanide, C₆H₄NH. NH. C: (NH). NH. C: (NH). NH₄. On digesting anilbiguanide with cyanamide it changes to phenylguanazole (see this), which is obtained from dicyandiamide and phenylhydrazine (B. 24, R. 649):

$$\begin{array}{c|c} C_{\delta}H_{\delta}NH-NH-C=NH\\ NH_{2}\\ NH \end{array} \longrightarrow \begin{array}{c|c} C_{\delta}H_{\delta}N-NH-C=NH\\ NH=C-NH \end{array} \qquad \text{n-Phenylguan-azole.}$$

Phenylhydrazine Derivatives of the Dicarboxylic Acids.—Oxalphenylhydrazilic Acid, C₈H₈NH.NH.CO.CO₂H, melting at 110° (A. 236, 197), and Oxalphenylhydrazide, (C₈H₈NH.NH.CO)₂ melting at 278°, correspond to oxanilic acid

Malonic acid has given the following phenylhydrazine derivatives: Malonic Ester Phenylhydrazide, Malonphenylhydrazilic ester, C₈H₅NH.NH.CO.CH₂.COOC₃H₅, melting at 90°, is produced when phenylhydrazine acts upon the chloride of malonic ester. It dissolves quite readily in caustic potash and from this solution hydrochloric acid precipitates malonylphenylhydrazide, 1-phenyl-3,5-pyrazolidone (formula below). Malonylphenylhydrazide, (C₈H₅NH.NH.CO)₂CH₂, melting at 187°, results from the interaction of malonamide and phenylhydrazine at 200° (B. 25, 1505). Ethylene succinic acid has yielded the compounds corresponding to those from malonic acid. Succ

interaction of malonamide and phenylhydrazine at 200° (B. 25, 1505). Ethylene succinic acid has yielded the compounds corresponding to those from malonic acid. Succinic phenylhydrazitic ester melts at 107°. Succinylphenylhydrazine results from the interaction of phenylhydrazine hydrochloride and succinyl chloride (B. 26, 2181). Succinyldiphenylhydrazide, (CH₂. CO. NH. NH. C₆H₆)₂, melts at 209° (B. 21, 2462). Anilsuccinimide, (CH₂CO)₂NNHC₆H₆, belongs in this category.

Phenylhydrazine Derivatives of Olefine Dicarboxylic Acids and Oxydicarboxylic Acids.

—Maleic anhydride and phenylhydrazine yield maleinphenylhydrazil. On boiling maleic or fumaric acid, dissolved in water, with an excess of phenylhydrazine, it adds itself as in the case of acrylic or crotonic acid (p. 126), and after the addition lactazam-formation ensues (B. 26. 117), and 1. phenyl-5-pyrasolidon-3-carboxylic acid results (see this).

ensues (B. 26, 117), and 1-phenyl-5-pyrazolidon-3-carboxylic acid results (see this).

Hetero-ring Formations of the Phenylhydrazine Derivatives of the Dicarboxylic

$$\begin{array}{c} \text{CO.NH.NH.C}_{6}\text{H}_{5} & \text{CO-NH} \\ \text{CO.OH} & \text{CO-NC}_{6}\text{H}_{5} & \text{Malonylphenylhydrazine, } \\ \text{CO.OH} & \text{CO-NC}_{6}\text{H}_{5} & \text{I-Phenyl-3,5-pyrazolidone} \\ \text{CH}_{2} \cdot \text{CO.Cl} & \text{CH}_{2} \cdot \text{CO.NH} \\ \text{CH}_{2} \cdot \text{CO. NH} & \text{Succinylphenylhydrazine} \\ \text{CH}_{2} \cdot \text{CO. NL} & \text{CH}_{2} \cdot \text{CO} & \text{NC}_{6}\text{H}_{5} \\ \text{CH}_{2} \cdot \text{COOH} & \text{CH}_{2} \cdot \text{CO} \\ \text{CH}_{3} \cdot \text{COOH} & \text{CH}_{2} \cdot \text{CO} \\ \text{CH}_{3} \cdot \text{COOH} & \text{NN.NC}_{6}\text{H}_{5} & \text{Anilsuccinimide} \\ \text{CH} \cdot \text{COOH} & \text{NH}_{8}\text{NH.C}_{6}\text{H}_{5} & \text{CO}_{3}\text{H. CHNH} \\ \text{CH}_{4} \cdot \text{COOH} & \text{CO}_{4}\text{H. CHNH} & \text{I-Phenyl-5-pyrazolidon-3-carboxylic Acid.} \\ \end{array}$$

HYDRAZIDINES OR AMIDRAZONES. FORMAZYL COMPOUNDS.

Two classes of compounds belonging to the amidines remain to be discussed at the conclusion of the phenylhydrazine derivatives of the carboxylic acids. The hydrazidines

A. Hydrazidines or Amidrazones. Ethenylphenylhydrasidine, CH_3 . $<<<_{NH_6}^{N.NHC_6H_5}$. The hydrochloride of this base is produced by the action of phenylhydrazine upon the 2385)

hydrochloride of acetimidoether (B. 17, 2002). Cyanamidrasone or Dicyanphenylhydrazine, NC-CN. NH. CoH, melting with decomposition at 160°, and Diamidrasme (B. 26, 2783 Anm.), or Cyanphenylhydrasine, (C₈H₈NH. N N_NH₂), melting at 225°, are produced when cyanogen acts upon phenylhydrasine. Dicyanphenylhydrasine is formed by the reduction of the HCN addition product of diazobenzene cyanide (p. 103), which probably, therefore, has the following formula: C₈H₅N : NCCN (B. 28, 2082). The constitution of cyanamidrazone is evident from its formation through the action of phenylhydrazine upon Flaveanhydride, NC—CSNH, and the constitution of diamidazone from its formation in the action of phenylhydrazine upon Rubeanhydride, S C (1, 437), and upon oxaldiamidoxime, HON NH₂ C (NOH NH₂) (B. 26,

Acetylamidrazone, pyroracemic acid phenylhydrazidine, CH, CO. CON. NHC, H, melting at 182°, is produced by reducing formazyl methylketone with ammonium salphide (B. 26, 2783).

Hetero-ring Formations with the Amidrazones.—The amidrazones condense with carboxylic acids, their anhydrides or chlorides to hetero-cyclic derivatives of the triandegroup (see this). Nitrous acid converts the amidrazones into tetrasole-derivatives (see these). Cyanamidrazone is changed by acetic anhydride to n-phenyl-3-cyan-5-methyltriacole; by nitrous acid to n-phenyl-3-cyantetrasole:

B. Formazyl compounds are obtained (1) from phenylhydrazones and normal diazonenzene usually in alkaline solution; (2) from phenylhydrazine and phenylhydrazine zides; the hydrazone-hydrazide produced at first oxidizes, under the influence of phenylhydrazine, with the loss of two hydrogen atoms; (3) from the phenylhydrazone chlorides, corresponding to the imide chlorides, by action of phenylhydrazine (B. 27, 320; **29**, 1386).

320; 29, 1380).

Formazyl Hydride, HC N: NC₆H₅, melting at 116° (1, 233), has been obtained from formazyl carboxylic acid by fusing it alone, or by boiling it with alcoholic potash.

Formazyl Methyl Ketone, CH₃. CO. C N: NC₆H₅, melting at 134°, results from

the action of diazobenzene upon acetone, acetoacetic ester, pyroracemic aldehyde hydra-

zone, and benzene azo acetyl acetone (B. 25, 3211).

Formazyl Carboxylic Acid, CO₂H . C N: N₅H₅
N . NH. C₈H₅, melting at 162°, is made by saponifying the ethyl formazyl carboxylic ester, melting at 117°. The latter is produced when diazobenzene chloride acts upon acetoacetic ester, oxaloacetic ester (B. 25, 3456), or upon phenylhydrazone-mesoxalic ester acid. Diformazyl,

$$\begin{array}{c|c} C_{\mathfrak{g}}H_{\mathfrak{g}}N: N \\ C_{\mathfrak{g}}H_{\mathfrak{g}}NH: N \end{array} \subset C \cdot C \begin{array}{c|c} N: NC_{\mathfrak{g}}H_{\mathfrak{g}} \\ N: NHC_{\mathfrak{g}}H_{\mathfrak{g}} \end{array}$$

greenish-brown, brilliant leaflets, melting at 226°. It results from the action of diazobenzene chloride upon lævulinic acid, hydrochelidonic acid, or acetone diacetic acid, and from dioxytartrosazone.

Formazylazobensene, Phenylazoformazyl, $(C_6H_5N=N)_2C=N$. NHC₆H₅, melting at 162°, results from the interaction of formazyl carboxylic acid or glyoxylic acid phenyl-

hydrazone and diazobenzene in alkaline solution (B. 25, 3457).

Hetero-ring Formations with the Formazyl Derivatives.—When concentrated mineral acids act upon the formazyl compounds, they split off aniline and *phentriazone* derivatives result; formazyl carboxylic ester yields a - Phentriazone (see this). By oxidation the formazyl-compounds change to tetrasolium derivatives; formazyl hydride yields n-Diphenyltetrazolium hydroxide:

$$\begin{array}{c|c} C_0H_5N & \longrightarrow N \\ C_0H_5NH-N & C\cdot CO_2C_2H_5 & \longrightarrow C_0H_4 & N=N \\ C_0H_5N & \longrightarrow N \\ C_0H_5NH-N & CH & \longrightarrow C_0H_5N(OH):N \\ C_0H_5NH-N & CH & \longrightarrow C_0H_5N(OH):N \\ C_0H_5NH-N & CH & \longrightarrow C_0H_5N(OH):N \\ C_0H_5NH-N & \longrightarrow C_0H_0N(OH):N \\ C_0H_0NH-N & \longrightarrow C_0H_0$$

16. Phenylnitrosohydrazine, $C_6H_5N < \frac{NO}{NH_4}$, or $C_6H_5NHNHNO$, yellowish-brown crystalline flakes, which readily change to diazobenzene imide (p. 110) (A. 190, 89), and are produced by action of nitrous acid upon phenylhydrazine. An excess of nitrous acid oxidizes phenylhydrazine to a diazobenzene salt (Ch. C. 1897, I, 381). Nitrotophenylsemicarbazide, C₆H₅N(NO)NHCONH₄, melting with decomposition at 127°, is obtained by the action of NO₂Na and acetic acid upon phenylsemicarbazide. It decomposes gradually at the ordinary temperature, more rapidly upon heating, with the production of phenylazocarbamide (p. 103). Diazobenzeneimide is obtained when it is boiled with caustic potash (B. 28, 1925).

16a. Tetrazones, derived from the hypothetical nitrogen hydride, NII₂ - N N - NH2, result upon oxidizing the unsym.-alkylphenyl- or diphenyl-hydrazines with mercuric oxide in alcoholic or ethereal solution, or by means of a dilute ferric chloride

solution:

$$2C_6H_6N(CH_3)$$
, $NH_2 + 2O = C_6H_5$, $N(CH_3)$, $N: N \cdot N(CH_3)$, $C_6H_5 + 2H_2O$.

They are solids, decomposed by fusion or upon boiling with dilute acids. Dimethyl diphenyl Tetrazone, C_8H_5 . $N(CH_3)N_2$. $N(CH_3)C_8H_5$, melts at 133°. Diethyldiphenyl Tetrazone melts at 108° (Å. 252, 281). Tetraphenyl Tetrazone, $(C_6H_5)_2N$. N_2 . $N(C_6H_5)_2$, from a-diphenylhydrazine, melts at 123°, and is colored blue by concentrated acids. The

tetrazones recall the osotetrazones (1, 328).
166. Hydrotetrazones, derived from the hypothetical hydride, NII, . NII . NII . NII₂, result upon oxidizing the aldehyde phenylhydrazones (B. 26, R. 55; 27, 2920)—e.g., benzal phenylhydrazone yields the compound, C₆H₅. CH: N. N. C₆H₅, dibenzal diphenyldihydrotetrazone, melting at 181° (B. 29, R. 591).

17. Buzylene or Diazohydrazo-compounds.—Hippurylphenylbuzylene, C₆H₅N =

N — NH — NHCO. CH₂. NH. CO. C₆H₅, melting at 84°, is an hippuric acid derivative of the unknown hydride, *Buzylene*, NH = N — NH — NH₂ (B. 26, 1268). It is formed from hippurylhydrazine and diazobenzene sulphate.

AROMATIC COMPOUNDS OF PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH, BORON, SILICON, AND TIN (1, 173-

The phenyl-derivatives of the elements just mentioned attach themselves to the aromatic nitrogen compounds. Their chlorides are most suitable for the preparation of these bodies. (1) They react with benzene at a red heat, hydrochloric acid being eliminated; (2) with benzene and aluminium chloride; (3) with mercury diphenyl; (4) with sodium and benzene chloride, or benzene bromide. This class of derivatives is produced also (5) from alloys of the elements with alkali metals and benzene haloids.

Phenyl Phosphorus Compounds.—Michaelis in 1876 succeeded, by the preparation of phosphenyl chloride, the starting-out substance for the obtainment of phosphenyl derivatives, in setting aside the experimental difficulties which opposed the union of the phenyl residue with phosphorus (A. 181, 265; 293, 193, 325; 294, 1). Some phosphorus phenyl compounds in composition correspond to known aromatic nitrogen-contain substances; the names of the respective phosphenyl bodies recall these:

 $\begin{array}{ll} C_6H_5PH_2, & Phenylphosphine \\ C_8H_5PO_2, & Phosphino-benzene \\ C_6H_6P: PC_6H_6, & Phospho-benzene. \end{array}$ Aniline, C₈H₅NH₂ Nitrobenzene, C₆H₅NO₂ Azobenzene, C₆H₅N: NC₆H₅ Phosphino-benzene

Phenylphosphine, C₆H₅. PH₂, phosphaniline, boiling at 160°, is obtained by the action of hydriodic acid and then alcohol upon phosphenyl-chloride, CaHa. PCl. It is a liquid possessing an extremely disagreeable odor. When exposed to the air, it oxidizes to phosphenyl oxide, C_gH_5 . PH_gO ,—a crystalline mass easily soluble in water. Phenyl-phosphine combines with HI to the iodide, C_gH_5 . PH_gI , out of which water again

separates phenylphosphine.

Phosphenyl Chloride, C₆H₅. PCl₂, boiling at 225° (corr.) with sp. gr. I.319 (29°), is a strongly refracting liquid which fumes in the air. It is formed (I) by conducting a mixture of benzene and PCl₂ vapors through tubes heated to redness (A. 181, 280); (2) by heating mercury diphenyl with PCl₂, and (3) by the action of AlCl₂ upon benzene and PCl₃. Aided by this last reaction the chlorphosphin-residue has also been introduced PCl₃. Aided by this last reaction the chlorphosphin-residue has also been introduced into dimethylaniline (B. 21, 1497), and into phenolalkyl ether (B. 27, 2559). It forms the tetrachloride, C₆H₅. PCl₄, with chlorine; this melts at 73°. With oxygen it yields the oxychloride, C₆H₅. PCl₂O, boiling at 260°, and with sulphur phosphenyl nulphochloride, boiling at 205° (130 mm.). When the dichloride is heated with water, we obtain phenyl-hypophosphorous acid, C₆H₅. PHO. OH, melting at 70°, while the tetrachloride forms phenylphosphoric acid, C₆H₅. PO. (OH)₃, which melts at 150°. p-Toly/phosphorchloride, CH₃[4]C₆H₄PCl₂, forms a tetrachloride, which forms with aniline tolyltrianilidophosphonium chloride, CH₃[4]C₆H₄P(NHC₆H₅)₅OI, melting at 245°. Sodium hydroxide converts the latter into the hydroxide, CH₃C₆H₄P(NHC₆H₅)₅OI, melting at 240° (B. 28. 2214).

melting at 240° (B. 28, 2214).

Phosphino-benzene, Collis PO2, melting at 1000, is obtained from phosphenyloxychloride

and phenylhypophosphorous acid (B. 25, 1747).

Phosphenyl chloride converts phenylphosphine into Phospho-benzene, CaHa.

P: P. C. II, melting at 150° (B. 10, 812).

Diphenylphosphine Chloride, (C₆H₅)₂PCl, boiling at 320°, is obtained from phosphenyl chloride alone at 280°, or with mercury diphenyl at 220° (B. 21, 1505). With phenol it yields *Phenoxyldiphenylphosphine*, (C₆H₅)₂POC₆H₅, boiling at 265-270° (62 mm.) (B. 18, 2118), and with dilute sodium hydroxide: diphenylphosphine, (C₆H₅)₂PH, boiling at 280°, and diphenylphosphinic acid, (C₆H₅)₂PO. OH, melting at

190° (B. 15, 801).

Triphenylphosphine, (C₆H₅)₃P, melting at 75° and boiling about 360°, is produced from C6H5. PCl2, and brombenzene, or from PCl3 and brombenzene by the action of sodium (B. 18, R. 562). It forms, with bromine, the dibromide, $(C_6H_6)_2PBr_9$, which is converted by water or alkalies into the dihydroxide, $(C_6H_5)_2P(OII)_2$. At 100° this passes into the oxide, $(C_6II_5)_3PO$. The latter melts at 143° and boils above 360°. Triphenylphosphin-oxide, $(C_6H_5)_3PO$, is isomeric with parioxyldiphenylphosphin- $(C_6H_5)_3PO$. Both companies in varor density determinations made with reduced (C₆H₅)₂POC₈H₅. Both compounds, in vapor density determinations made with reduced pressure (1, 29), yield values according with the simple molecular formulas. phorus, therefore, in the first body is quinquivalent, and in the second it is trivalent (Michaelis and La Coste, B. 18, 2118).

Phenyl Arsenic Compounds.—Reactions similar to those used in obtaining the phenyl substitution products of phosphorous chloride have been used with arsenic, and the following bodies have been obtained: Phenyl arsenious chloride, $C_6H_6AsCl_1$; Diphenyl arsenious chloride, $(C_6H_5)_2AsCl_1$; Triphenyl Arsine, $(C_6H_5)_2As$; Arsenobenzene, C_6H_5As : As C_6H_5 . (A. 201, 191; 207, 195; 270, 139; B. 19, 1031; 25, 1521; 27,

263).

Triphenyl Stibine, (C₈H₅)₂Sb, melting at 48°, is produced on introducing sodium

into a solution of 40 grams of chlorbenzene and 40 grams of antimonious chloride in benzene (A. 233, 43).

Bismuth Triphenyl, (C₆H₅)₃Bi, melting at 78°, is prepared by heating bromben-

zene and bismuth sodium (A. 251, 324).

Phenyl Boron Compounds.—Phenyl boron chloride, C. H. BCl2, melting at 0° and

Phenyl Boron Compounds.—Phenyl boron chloride, C₆H₅BCl₂, melting at 0° and boiling at 175°, and diphenylboron-chloride, (C₆H₅)₂BCl, boiling at 271° (B. 27, 244), result from the interaction of mercury diphenyl and boron chloride.

Phenyl Silicon Compounds.—Phenyl-ailico-chloride, C₆H₅. SiCl₃, is prepared by heating mercury diphenyl and SiCl₄ to 300°. It boils at 197° (Ladenburg, A. 173, 151). Water decomposes it into silico-benzoic acid, C₆H₅. SiO. OH, melting at 92°. Alcohol forms the triethyl ether, C₆H₅. Si(O. C₂H₆)₃, boiling at 137°. Zinc ethyl converts the chloride into triethyl-phenyl-silicide, C₆H₅. Si. (C₂H₅)₃, boiling at 230°.

Tetraphenyl Silicon, Si(C₆H₅)₄, is produced by the action of sodium upon a mixture of SiCl₄, chlorbenzene, and ether (B. 19, 1012). It melts at 228° and distils beyond 300°.

beyond 300°.

Phenyl Tin Compounds.—Mercury diphenyl and stannic chloride interact to form

Tin Diphenyl Chloride, $(C_8H_5)_2$ SnCl₂, melting at 42° (A. 194, 145).

Tin Tetraphenyl, Sn($C_8H_5)_4$, is produced by the action of tin sodium upon brombenzene. It melts at 226° and boils above 420° (B. 22, 2917).

5. PHENYL METAL DERIVATIVES (1, 182).

The phenyl group has been combined with magnesium, mercury, and lead.

Magnesium Diphenyl, (C₄H₅)₂Mg, is a light, yellowish-white powder, dissolving readily in a mixture of benzene and ether. It is produced on heating mercury diphenyl

with magnesium powder and some acetic ester to 180-185° (A. 282, 320).

Mercury-phenyl, (C₈H₅)₂Hg, melting at 120°, is formed by treating brombenzene in benzene solution for some time with liquid sodium amalgam (Otto and Dreher, A. 154, 93); the addition of some acetic ether facilitates the reaction. It crystallizes in colorless, rhombic prisms, and can be sublimed. It assumes a yellow color in sunlight. It dissolves readily in benzene and carbon disulphide, but with more difficulty in ether and alcohol; in water it is insoluble. When distilled it decomposes for the most part into diphenyl, benzene, and mercury. Acids decompose it with formation of benzene and mercury salts. Haloid compounds are produced by the action of the halogens—e.g., Mercury-phenyl chloride, C₆H₆HgCl, melting at 250°; mercury-phenyl bromide, C₆H₆HgBr, melting at 275°; mercury-phenyl iodide, C₆H₆HgI, melting at 265°. Mercury-phenyl indide, C₆H₆HgI, melting at 265°. cury-phenyl hydroxide, C₆H₅HgOH, is produced when silver oxide and alcohol act upon the chloride (J. pr. Ch. [2] 1, 186).

Mercury Dialphyls: See A. 173, 162; B. 14, 2112; 17, 2374; 20, 1719; 22,

1220, etc.

Lead Tetraphenyl, (C₆H₅)₄Pb, is formed by heating brombenzene with lead sodium and acetic ether. It melts at 224° (B. 20, 3331).

6. SULPHO-ACIDS.

The ease with which sulpho-acids are produced distinguishes the aromatic hydrocarbons from the aliphatic bodies to the same degree that marks their easy nitration. The introduction of a sulpho-group in the place of aromatic hydrogen atoms is termed "sulphonation.

Formation.—(1) The sulphonic acids of the benzene hydrocarbons (as well as of other benzene derivatives) are very easily obtained by mixing (or digesting) the latter with concentrated or fuming sulphuric acid. In this manner it is possible to combine three sulpho-groups with one benzene nucleus:

$$C_6H_6 + HO \cdot SO_2H = C_6H_6 \cdot SO_2H + H_2O$$
.

(2) In the action of an excess of chlorsulphonic acid, Cl. SO₂OH, the principal products, with careful cooling, are the chlorides of the sulpho-acids (B. 12, 1848; 28, 2172). The reaction then proceeds in the following way (B. 22, R. 739):

$$\begin{aligned} &C_{\mathbf{c}}H_{\mathbf{d}} + \text{CISO}_{\mathbf{2}}\text{OH} = \text{HCl} &+ C_{\mathbf{c}}H_{\mathbf{b}}.\text{SO}_{\mathbf{2}}\text{OH} \\ &C_{\mathbf{c}}H_{\mathbf{b}}\text{SO}_{\mathbf{d}}\text{OH} + \text{CISO}_{\mathbf{1}}\text{OH} = H_{\mathbf{c}}\text{SO}_{\mathbf{d}} + C_{\mathbf{c}}H_{\mathbf{b}}\text{SO}_{\mathbf{c}}\text{CI}. \end{aligned}$$

Sulphones are secondary products (p. 139).

(3) Further, sulphonic acids can be obtained from the diazo-amido-derivatives by boiling with sulphurous acid (p. 110).

(4) By the oxidation of thiophenols (p. 156). This reaction proves that the sulphur atom of the sulpho-group is in union with the aromatic nucleus (compare mercaptans) (1, 148).

(5) By the oxidation of sulphinic acids (p. 138).

Properties and Transformations.—Many aromatic sulpho-acids are very soluble in water and crystallize with difficulty. They can be separated from aqueous solution in the form of their sodium salts by means of sodium chloride: salting out (B. 28, 91). The ready solubility of the sulpho-acids, in conjunction with their easy production, meets with an important technical application in the conversion of aromatic dyes insoluble in water into their sulpho-acids, which dissolve in water with ease.

(1) The chlorides of the acids are made by acting upon the alkali salts with POCl₃ and PCl₅, and from the acids themselves by the action of PCl₅. The chlorides are converted into amides, esters, etc., as indicated under the alkyl sulphonic acids (1, 152). The esters of the sulphoacids are transposed by alcohol at 140-150°, with the production of ethers (1, 133). The sulphonamides are stable and crystallize well; they are frequently prepared for the characterization of a sulpho-acid.

(2) Hydrocarbons (together with phenyl sulphones) are formed when

the free acids are subjected to distillation:

$$C_6H_5$$
. $SO_3H = C_6H_6 + SO_3$.

This rupture is more easily accomplished by heating the acids with concentrated HCl to 150°, or by distilling the ammonium salt of the sulphonic acid, or a mixture of the lead salt with ammonium chloride (B. 16, 1468). The decomposition results with least difficulty by conducting steam into the dry sulpho-acid, or its solution in concentrated sulphuric acid; superheated steam is most effective (B. 19, 92).

(3) The SO₂Cl group in the sulpho-chlorides can be replaced by chlorine through the action of PCl₅. In some sulphonic acids free chlorine and bromine are capable of eliminating the sulpho-group and introducing the halogens (B. 16, 617).

(4) The sulpho-group in many sulphonic acids is often replaced by NO₃ upon treating

them with concentrated nitric acid.

(5) Anilines result from the action of sodamide, NH2Na, upon benzene sulphonates (B. 19, 903):

$$C_6H_5$$
. $SO_3Na + NH_2Na = C_6H_5$. $NH_2 + SO_3Na_2$.

(6) The sulphonic acids of the alkyl benzenes, more frequently applied in the form of their sulphamides, yield sulphocarboxylic acids upon oxidation. The oxidation of o toluene sulphamide to the sulphinide of o sulphobenzoic acid (see this), called saccharin, is technically important.

(7) The chlorides of the aromatic sulpho-acids become thiophenols upon reduction:

$$C_0H_0SO_2CI + 6H = C_0H_0SH + 2H_2O + HCI.$$

This reaction, like that of the oxidation of thiophenols to sulphonic acids, demonstrates that in the sulpho-acids the sulphur is in immediate union with the benzene nucleus

(8) The sulphonic acids are not decomposed upon boiling them with aqueous alkalies. Phenols are formed when they are fused with alkalies, This reaction serves for the technical preparation of resorcinol (p. 160) and other phenols:

$$C_aH_a$$
. $SO_aK + KHO = C_aH_aOH + SO_aK_a$.

(9) When distilled with potassium cyanide (or dry yellow prussiate of potash) nitriles result:

$$C_aH_b$$
. $SO_aK + CNK = C_aH_b$. $CN + SO_aK_a$

and these may be readily saponified to carboxylic acids. This reaction answers for the synthesis of aromatic acids from the hydrocarbons.

(10) Carboxylates are also obtained on fusing the alkali sulphonates with sodium formate.

Monosulphonic Acids.—Benzene Sulphonic Acid, C6H5. SO3H, melting at 50°, crystallizes from water, in which it is exceedingly soluble, in plates containing water of crystallization.

The barium salt, (C₂H₅.SO₂)₂Ba + H₂O, forms pearly leaflets, and is sparingly soluble in alcohol.

The chloride, C₆H₅. SO₂Cl, melts at 14.5°, boils at 116° (B. 25, 2257), and has specific gravity of 1.378 at 23°. It slowly reverts to the acid upon boiling with water. The ethyl ester, boiling at 156° (15 mm.), obtained by the action of ethyl alcohol on the chloride, is decomposed into benzene sulphonic acid and ethyl ether (I, 133) when it is heated to 150° with ethyl alcohol.

Benzenesulphamide, C₆H₅, SO₂, NH₄, melts at 150°.

Benzene Sulpho-nitramide, C₆H₆SO₂NHNO₂, consists of colorless plates, readily soluble in water. It decomposes at 100° into benzene sulphonic acid and nitrous oxide. It is formed when a mixture of nitric and sulphuric acids acts upon benzenesulphamide. Its potassium salt, C₆H₆SO₂NK . NO₂, melts at 275°, and when reduced by glacial acetic acid and zinc dust becomes benzene sulphon-hydraside, C₆H₆SO₂NH . NH₂. The sulphamide and nitrous acid yield dibenzene sulphon-hydraylamine, (C₆H₆SO₂)₂NOH, which can also be made by the interaction of benzene sulphinic acid and sodium nitrite; with diazobenzene chloride the product is benzene-sulpho-diazobenzene amide,

C₆H₅SO₂NH — N = N. C₆H₅, melting with decomposition at 101° (B. 27, 598).

Benzsulph-hydroxamic Acid, C₆H₆SO₂. NHOH, melting at 126°, is obtained from benzene sulphochloride and hydroxylamine. Alkalies decompose it into benzene sulphinic acid and hyponitrous acid (B. 29, 1559, 2324):

$$2C_aH_aSO_aNHOH + 2KOH = 2C_aH_aSO_aK + (NOH)_a + 2H_aO.$$

Toluene Sulphonic Acids.—In sulphonating toluene o- and p-acids are the chief The o-acid can be obtained from p-tolylhydrazine-o-sulphonic acid free from the p-acid. The m-acid is obtained from p-toluidine-m-sulphonic acid. o- Toluene Sulphothe p-acid. The m-acid is obtained from p-totulatine-m-sulphonic acid. O- totuene Sulpho-chloride is a liquid. o-Toluene-sulphomide melts at 155° (see o-sulphobenzoic acid). m-Toluene-sulphonic Acid, $CH_3[1]C_6H_4[3]SO_3H + H_2O$; its chloride is a liquid; its amide melts at 107° . p-Toluene-sulphonic Acid, $CH_3[1]C_6H_4[4]SO_3H + 4H_2O$, melts at 92° ; its chloride melts at 69° and boils at 145° (15 mm.); its bromide melts at 96° , its iodide at 84° , and its amide at 137° . Ditoluene sulph-hydroxamic acid, $(C_7H_7.SO_2)_3NOH$, melts with decomposition at 148° . It results from the action of sodium nitrite upon toluene-sulphinic acid. It combines with an additional molecule of the sulphinic acid to Tritoluene Sulphonamide, (C,H, . SO2),N, melting at 1900 (J. pt.

Ch. [2] 54, 95).

Xylene Sulphonic Acids .- 1,2-Xylene-4-sulphonic Acid; its chloride melts at 51°, its amide at 144. 1,3-Xylene-4-sulphonic Acid; its chloride melts at 34° and its amide at 137°. 1,3-Xylene-2-sulphonic Acid: its amide melts at 95°. 1,4-Xylene-3-sulphonic Acid: its chloride melts at 25° and its amide at 247°. They result upon sulphonating the various xylenes.

[1,2,4]-Pseudocumene-5-sulphonic Acid, (CH₃)₃C₆H₂SO₂H + 2H₃O, melts at 111°. Its chloride melts at 61° and the amide at 181°. Mesitylene Sulphonic Acid,

CaHieSOa + 2HeO, melts at 77°, its chloride at 57°, and its amide at 141°.

Polysulphonic Acids.—Benzene-disulphonic Acids, C₈H₄ SO₈H. benzene with fuming sulphuric acid to 200° C., we get meta- and para-benzene disulphonic acids, with the former in predominating quantity, but by prolonged heating it passes into the para-variety (B. 9, 550). Meta-disulphonic acid (1,3) is produced from disulphanilic acid (p. 137) by means of the diazo-compound.

Orthobenzene disulphonic acid is formed from meta-amidobenzene sulphonic acid by further introduction of the sulpho-group, and replacement of NH₂ by hydrogen. The melting points of the sulpho-chlorides and sulphamides of the three isomeric disulphonic

acids are:

The corresponding dicyanides, CaH4(CN)2, the nitriles of the three phthalic acids, are obtained by distillation with potassium cyanide or potassium ferrocyanide. When fused with potassium hydroxide, both meta and para acids yield resorcinol (metadioxybenzene); at lower temperatures metaphenol-sulphonic acid, CaH4(OH)SOaH, results at first from both acids.

Benzene-trisulphonic Acid, Call (SO3H) (1,3,6), is easily made by heating potassium m-benzene disulphonate with common sulphuric acid (B. 21, R. 49). The free acid (from the lead salt) crystallizes in long needles with 3H₂O; its *chloride* melts at 184°, its *amide* at 306°. Fused with caustic potash it yields *phloroglucin*, C₆H₂(OII), and upon heating with potassium cyanide it forms the nitrile, which upon saponification

becomes trimesic acid, C₆H₃(CO₂H)₂.

Toluene Disulphonic Acids.—The six possible isomerides are known (B. 20, 350;

29, R. 868). Xylene Disulphonic Acids (B. 25, R. 790).

Chlor-, Brom-, Iod-, Iodoso-, Nitro-, Nitroso-, and Amidobenzene Sulphonic Acids.—The chlor-, brom-, and iod-benzene sulphonic acids are prepared from the three amidobenzene sulphonic acids by means of the diazo-reactions (B. 28, 90). p-Compounds are the principal products in the sulphonation of chlor- and brom-benzenes. In nitrating benzene-sulphonic acid and sulphonating nitro-benzene the three isomeric nitro-benzene-sulphonic acids are produced with the m-derivatives in predominating quantity (A. 177, 60).

The following table contains the melting points of the chlorides and amides of the acids:

	ORTHO.		ME	TA.	PARA.		
Chlorsulpho	Chloride. 28° 51°	Amide. 188° 186°	Chloride. Oil	Amide. 148° 154°	Chloride. 53° 75°	Amide. 143° 166°	
Iodsulpho Nitrosulpho	51° 67°	170° 186°	23° 60°	152° 161°	84° Oil	181°	

o-lod-chloride-bensene sulphochloride, ICl, [2]C, H, [1]SO, Cl, melting at 60°, is con-

verted by sodium hydroxide into iodoso-benzene-sulphonic acid (B. 28, 95).

The compounds resulting from the action of hydriodic acid upon the nitrobenzenesulpho-chlorides, CaH4(NO2)SO2Cl, and formerly regarded as sulphimidobensenes, C₈H₄<8H₅>, represent nitrodiphenyldisulphides, (C₈H₄. NO₂)₂S₂ (B. 21, 1099). m-Nitrosobensene-sulphonic Acid (B. 25, 75).

Amidobensene-sulphonic Acids.—The three acids are produced by the reduction of the three nitrobenzene sulphonic acids. On sulphonating aniline at 180° with fuming sulphuric acid (8-10 per cent. SO₁), the p-derivative constitutes the chief product. It is sulphanilic acid, important in the technology of dyes, and was discovered in 1845 by Gerhardt. The second sulpho-group enters the o-position with the formation of 1-aniline-2,4-disulphonic acid or disulphanilic acid; a trisulphonic acid has not been produced (B. 23, 2143). The amidobenzene-sulphonic acids, like glycocoll (1, 354) and taurine (1, 306) can be regarded as cyclic ammonium salts: C₈H₆ NH₈.

The three amido-benzene sulphonic acids dissolve with difficulty in water, alcohol, and ether. The (ortho)-acid either crystallizes in anhydrous rhombohedra or in foursided prisms containing ½H₂O; these do not effloresce. It is best prepared by the reduction of p-brom-aniline-o-sulphonic acid (B. 28, R. 751; 29, 1075). The (1,3)acid, called metanilic acid, and also important in the technology of dyes, crystallizes

in delicate needles or in prisms with 1 ½ H₂O, which effloresce.

Sulphanilic Acid crystallizes from hot water in rhombic plates with 1 molecule H₂O; these effloresce in the air. They are soluble in 112 parts H₂O at 15° (B. 14, 1933). It yields a considerable quantity of quinone when oxidized with MnO₂ and H₂SO₄ or chromic acid. It yields aniline and not amidophenol when fused with caustic potash; unlike its isomerides it is readily converted by bromine water into tribromani-

line (B. 29, R. 309).

The sodium amido-benzene-sulphonates yield acetyl derivatives with acetic anhydride (B. 17, 708), whereas the free acids are not in condition to do this. This fact argues for the ammonium salt formula of the three acids.

Diazobenzene-sulphonic Acid Anhydrides, Cyclic Diazides.-Nitrous acid transforms the three amido-benzene-sulphonic acids into the anhydrides of the diazobensene-sulphonic acids:

 $C_{\!_{\boldsymbol{0}}}H_{\!_{\boldsymbol{4}}}\!\!<^{SO_{\!_{\boldsymbol{2}}}}_{N_{\!_{\boldsymbol{2}}}}\!\!>\!\!O$ $C_{\bullet}H_{\bullet} < SO_{\bullet}OH N_{\bullet}OH$ Diazobenzene-sulphonic Acid

The hydrated sulpho-acids are not known; they pass at once into anhydrides. The di-potassium and the di-sodium salts of the o- and p-diazobenzene sulphonic acids, CaH₄(SO₂Me)(N₂OMe), exist each in two forms, one of which belongs to the normal and the other to the isodiazo-series (p. 101). The iso-salts are produced on digesting the and the other to the isodiazo-series (p. 101). The iso-salts are produced on digesting the normal salts; they give up nitrogen less readily and do not combine, or at least with difficulty, with aromatic amines or phenols, to yield azo-dyes (B. 29, 1059, 1388). Primary Polassium Isodiazosulphomate, C₆H₄(SO₂K)N₂OH + H₂O, results on treating the corresponding dipotassium salt with acetic acid (B. 28, 1386). A bleaching lime solution oxidizes the diazide of sulphanilic acid to the compound C₆H₄(SO₂H)N₂O₃H, which must probably be regarded as an oxynitramine, C₈H₄(SO₃H)N(OH)NO₂ (B. 29, 2948). It is rather remarkable that, while otherwise it is only the ortho-compounds of the

benzene di-derivatives which form inner anhydrides, all three of the diazobenzene sulphoacids are capable of anhydride formation. They exhibit all of the reactions of the

diazo-compounds.

The diaside of sulphanilic acid, p-diazobenzene-sulphonic acid, consists of sparingly soluble, white needles; heated with absolute alcohol, it forms benzene-sulphonic acid; with water the diazo-acid becomes p-phenol-sulphonic acid; while with potassium sulphide the di-potassium salt of p-thiophenolsulphonic acid results.

Amido-azo-benzene-sulphonic Acids.—The diazides of sulphanilic acid and

metanilic acid are used in the manufacture of sulphurized anodyes: The first group of

this great class of dyes has received mention (p. 114); it comprises the amido-accompounds, which are insoluble or dissolve with difficulty in water. Upon introducing the sulpho-group into the amido-azo-derivatives it will be discovered that the solubility in general increases with the number of sulpho-groups. The alkali salts of the amido-azo-benzene-sulphonic acids constitute the dyes soluble in water. We shall meet with other groups of azo-dyes when we study the phenols: oxyazo-compounds. The naphthalene-azo-compounds and the benzidine-dyes, containing the diphenyl residue, are especially important.

Arbitrary names are assigned these dyes, with the addition of the letters Y (yellow), O (orange), and R (red), whose number approximately expresses the intensity of the

color. They color wool and silk directly, cotton after it has been mordanted.

Formation.—(1) The amido-azo-bodies are sulphurized. (2) The diazides of sul-

phonic acids are combined with bases.

Upon sulphonating amido-azobenzene there results a mixture of amido-azobenzene mono- and di-sulphonic acids, known in commerce under the names acid yellow or pure yellow: SO₃H[4]C₆H₄[1]N = N[1']C₆H₄[4']NH₂ and SO₃H[4]C₆H₄[1]N = N[1']C₆H₄[4']NH₂[3']SO₃H (B. 22, 847). Being amido-bodies the sulpho-acids are themselves capable again of diazotizing and combination, whereby very valuable dyes have been obtained (compare Biebrick scarlet).

The following azo-dyes have been made by combining the diazide of sulphanilic acid with dimethylaniline and diphenylamine, and the diazide of metanilic acid with

diphenylamine:

[4']-Dimethylamido-azo-bensene-[4]-sulphonic acid, SO₂H[4]C₈H₄[1]N = N[1]C₈. H₄[4']N(CH₂)₂, melting at 112°, consists of golden-yellow leaflets (B. 10, 528; 12, 1490). Its sodium salt, as a dye, bears the names tropzoline O, orange III, and helianthine. It serves as a delicate indicator in alkalimetry; mineral acids convert the alkaline orange-colored solution into a rose-red. CO₂, H₂S, and acetic acid do not act on it in the cold (Ch. Z., VI, 1249; B. 18, 3290). By reduction helianthine yields sulphanilic acid and para-amido-dimethyl aniline (p. 95).

[4'] Phenylamido azobenzene [4] sulphonic Acid, SO₂H[4]C₆H₄[1]N = N[1]C₆H₄. [4']NHC₆H₅. Its sodium salt dyes wool and silk a beautiful orange, and as a dye is known by the names tropxoline OO, orange IV. It is used as an indicator in alkalimetry (B. 16, 1989). By decomposition it yields sulphanilic acid and p-amido-diphenyl-

amine.

[4']-Phenylamido-azobenzene-[3]-sulphonic Acid is formed from metanilic acid and

bears the name metanil yellow.

Phenylhydrazine Sulphonic Acids are produced upon reducing the diazides of aniline sulphonic acids with sodium sulphite or stannous chloride (B. 22, R. 216), and by the direct action of concentrated sulphuric acid upon phenylhydrazines (B. 18. 1872).

by the direct action of concentrated sulphuric acid upon phenylhydrazines (B. 18, 3172).

Phenylhydrazine-p-sulphonic Acid, C₆H₄. (NH. NH₂)SO₅H, is not readily soluble in water. It is used in the preparation of tartrazine (vol. 1), having the following N—NHC₆H₄SO₃Na

constitution: CO₂NaC — CO

N — NC₈H₄SO₃Na.

Hydrazobenzene-m-disulphonic Acid, SO₃H[3]C₆H₄[1]NH — NH[1]C₆H₄[3']SO₅H, has been prepared by the reduction of m-nitrobenzene sulphonic acid, and is converted into benzidine disulphonic acid by hydrochloric acid (B. 21, R. 323; 23, 1053).

Sulphinic Acids (compare 1, 153).—Formation: (1) By the action of zinc dust upon the ethereal solution of the sulphonic acid chlorides; (2) from the latter and thiophenol salts:

$$C_6H_5SO_2Cl + 2C_6H_5SNa = C_6H_5SO_2Na + NaCl + (C_6H_5S)_2;$$

(3) from SO₂ and benzene in the presence of aluminium chloride (B. 20, 195); (4) by the action of sodium upon the sulphones (B. 26, 2813); (5) by the decomposition of the benzene sulph-hydroxamic acids (p. 135).

Deportment.—The sulphinic acids are not very stable, and when heated with water,

split up into sulphonic acids and disulphoxides.

The air and oxidizing agents (especially BaO₂) convert them into sulphonic acids. Their salts unite with sulphur, forming thiosulphonates. When fused with alkalies, they decompose into benzenes and alkaline sulphites.

Benzene sulphinic acid and quinone unite to unsym. -p-dioxydiphenylsulphone, (HO)₂-

[2,5]C₆H₃[1]SO₃C₆H₅ (B. 27, 3259); it also reacts with a number of other substances containing quinoid linkages (compare B. 29, 2019).

Their alkali salts and alkyl iodides yield mixed sulphones, and with chlorcarbonic esters they form the real sulphinic esters (B. 26, 308, 430):

$$C_aH_bSO_2Na + ClCO_2C_2H_b = C_aH_b$$
. $SOOC_2H_b + NaCl + CO_2$.

Benzene Sulphinic Acid, C₂H₅. SO. OH, melts at 83°. Zinc Salt, (C₂H₅SO₂)₂-Zn + 2H₂O. Ethyl Ester, sp. gr. I.141 (20°), decomposes when it is heated.

o Toluene Sulphinic Acid, C₂H₄[1](CH₂)[2]SOOH, melts at 80° (J. pr. Ch. 54,

517). Benzene Thiosulphonic Acid.—Its salts result from the chloride of benzene sulphonic acid and alkali sulphides, as well as from the interaction of benzene sulphinates

and sulphur (B. 25, 1477).

Disulphoxides or Esters of the Thiosulphonic Acids.—Alkyl esters and alkylen esters of benzene thiosulphonic acid result from the interaction of the potassium salt with

the corresponding bromides (B. 25, 1477).

Phenyl esters—e.g., C₆H₅. SO₂. S. C₆H₅—are obtained (1) by oxidizing the thiophenols with nitric acid, and (2) by heating the sulphinic acids with water to 130°.

Benzene Disulphoxide, C₆H₅. SO₂. S. C₆H₅, melting at 45°, is insoluble in water, but dissolves readily in alcohol and ether (B. 20, 2090).

Sulphobenzene Sulphide, (C₈H₈SO₂)₂S, melting at 133°, and Sulphobenzene Disulphide, (C₈H₈SO₂)₂S, melting at 70°, result from the action of iodine and of chlorine upon potassium benzene thiosulphonate (B. 24, 1141).

Diphenylsulphoxide, Thionyl Benzene, (C₈H₈)₂SO, melting at 70°, is produced by the action of SO₂ or SO₂Cl₂ upon benzenes in the presence of AlCl₈ (B. 20, 195; 27,

Potassium permanganate oxidizes it to diphenyl sulphone.

Diphenylselenium Oxide, (C₆H₆)₂SeO, has been prepared by oxidizing diphenylselenide (see this), or from the dibromide of the latter (B. 29, 424).

Sulphones.—The alkylalphyl sulphones are isomeric with the esters of the alkyl sulphinic acids. They result from the sodium sulphinates and the alkylogens. The purely aromatic sulphones are obtained (1) by the action of SO₃ or chlorsulphonic acid upon benzenes (together with sulphonic acids), ${}_{2}C_{6}H_{6} + {}_{3}C_{6} = (C_{6}H_{5})_{2}SO_{2} + H_{2}O$; (2) by the distillation of sulphonic acids (together with benzenes); (3) by the oxidation of the phenyl sulphides; (4) on heating benzene-sulphonic acids with benzenes and $P_{2}O_{5}$; (5) by the action of zinc dust or aluminium chloride upon a mixture of the sulphonic chlorides and benzenes:

$$C_{6}H_{5}SO_{2}CI + C_{6}H_{5}CH_{3} \longrightarrow CH_{3}[1]C_{6}H_{4}[4] SO_{2}CI.$$

The same phenyl p-tolyl-sulphone results from benzene sulphonic acid and toluene as from p toluene-sulphonic acid chloride and benzene, which would prove that both groups are in union with sulphur and that the latter is sexivalent (B. 11, 2181); (6) oxy and amido-substituted sulphones result from the union of sulphinic acids with quinone and

quinone imide derivatives (B. 29, 2024).

Phenylethyl Sulphone, C₆H₅SO₂C₂H₅, melts at 42° and boils above 300°. Phenylethyl Sulphone Alcohol, C₆H₅. SO₂. CH₂. CH₂OH, is a syrup formed from ethylene chlorhydrin and sodium benzene sulphinate, as well as by the action of concentrated sodium hydroxide upon ethylene diphenyl disulphone, $C_6H_6SO_2$, CH_2 , CH_2 , CG_2 , C_6H_6 , melting at 180°. Phenyl sulphone ethyl alcohol upon oxidation yields phenyl sulphone acetic acid, $C_6H_6SO_2$, CH_2 , CO_2H_3 , melting at II2°; caustic potash resolves this into CO_2 and phenyl methyl sulphone, C_6H_6 , SO_2 , CH_3 , melting at 88°. The hydrogen of the CH_3 -group in the esters of phenyl-sulphone acetic acid is, indeed, replaceable by sodium but not by alkyls (R_2 22 1447; 22 1647). Phenyl Allyl Sulphone C W_3 sodium, but not by alkyls (B. 22, 1447; 23, 1647). Phenyl Allyl Sulphone, C.H. SO, . C, H, is an oil (A. 283, 185).

The a- and β -phenyl-sulphone propionic acids, melting at II5° and I23° (B. 21, 89),

as well as numerous other mixed fatty-aromatic sulphones of the greatest variety, have also been prepared. The phenyl groups have also been replaced by tolyl groups.

Diphenylsulphone, (C₆H₅)₂SO₂, Bensene Sulphone, Sulphobenside, melting at 128° and boiling at 276°, is formed by the distillation of benzene sulphonic acid, and by the oxidation of phenyl sulphide, (C₆H₅)₂S, and diphenylsulphazide (see above); further, from benzene sulphonic chloride, C₆H₅. SO₂Cl, and mercury diphenyl, as well as from benzene and benzene sulphonic chloride or sulphuryl chloride with aluminium chloride (B. 26, 2940). It is also obtained by the action of furning sulphuric acid or SO₂ upon benzene. It is converted into benzene-sulphonic acid when digested with concentrated sulphuric acid. When heated with PCl₅, or in a current of chlorine gas, it is decomposed into chlorbenzene and the chloride of benzene sulphonic acid.

With sulphur or selenium it forms the diphenylsulphone: Diphenylsulphide or diphenylselenide (B. 27, 1761). Sodium converts it into sodium benzene sulphinate and diphenyl (B. 26, 2813). Diphenyl Selenone, (C₆H₅)₂SeO₂, melting at 155° and boiling at 271°, results on oxidizing diphenyl selenium oxide with potassium permanganate

(B. 29, 424).

7. PHENOLS.

The phenols are derived from the aromatic hydrocarbons by the replacement of hydrogen of the benzene residue by hydroxyl. The phenols, like the alcohols, are distinguished as mono-, di-, and trihydric, according to the number of hydroxyl groups which have entered. All of the six hydrogen atoms in benzene can be substituted by hydroxyl The phenols correspond to the tertiary alcohols, as they yield neither acids nor ketones upon oxidation. Their acid nature, distinguishing them from alcohols, is governed by the more negative nature of the phenyl group, and is enhanced by the entrance of more negative groups (see picric acid, p. 150). In contrast to the phenols the aromatic alcohols, which are their isomerides, and have hydrogen of the side-chains replaced by hydroxyl, approach the aliphatic alcohols in their deportment.

Various representatives of the phenols have been found in the vegetable kingdom.

Some of them occur already formed as phenol-sulphonic acids in the urine of mammalia. In the organism of the latter many organic bodies are oxidized to phenols: benzene to phenol, brombenzene to bromphenol, aniline to amidophenol, phenol to hydroquinone. In the decay of albumin the presence of phenols has also been established.

Phenols are produced in the dry distillation of wood, particularly beech-wood, turf, bituminous coal (B. 26, R. 151), and anthracite coal.

To isolate the phenols from coal tar shake the latter with caustic alkali in which they are soluble. Acids liberate them from this solution, and then they can be purified by fractional distillation.

MONOHYDRIC PHENOLS.

In addition to the methods of formation just given, the following are worthy of note:

(1) The decomposition of the diazo-derivatives, especially their sulphates, with boiling water (p. 105).

(2) Fusion of the sulphonic acids with potassium or sodium hydroxide. This reaction was discovered in 1867 by Kekulé, Würtz, and Dusart, independently of each other:

$$C_6H_6$$
. $SO_3K + KOH = C_6H_6$. $OH + SO_3K_2$.

In practice this method is used to obtain phenols from sulphoacids, the operation being carried out in iron vessels.

The experiment in the laboratory is executed in a silver or nickel dish, the fusion supersaturated with sulphuric acid, and the phenol extracted by shaking with ether.

In fusing sulphonic acids or phenols containing halogens, the latter are also replaced with formation of polyhydric phenols. Occasionally the sulpho-group splits off as sulphate and is replaced by hydrogen; thus, cresolsulphonic acid yields cresol.

(3) The halogen benzene substitution products do not react with alkalies; but if nitro-groups are present at the same time, the halogens are replaced even by digesting with aqueous alkalies—this will occur the more readily if the nitro-groups be multiplied. In this respect they approach the acid chlorides:

$$C_0H_2(NO_2)_3CI + H_2O = C_0H_2(NO_2)_3OH + HCI$$

Picryl Chloride Picric Acid.

(4) The amide-group in the nitroamido-derivatives can also be replaced by hydroxyl on boiling with aqueous alkalies; ortho- and para-nitranilines, $C_6H_4(NO_2)$. NII, (not meta), yield their corresponding nitrophenols. The ortho-dinitro-products react similarly (n - 67)

(5) Small quantities of phenol can be obtained from benzene by the action of ozone, hydrogen peroxide (palladium hydride and water), and by shaking with sodium hydroxide and air (B. 14, 1144). By the addition of oxygen to benzene through the instrumentality of aluminium chloride.

(6) By the breaking down of phenol carboxylic acids, when their salts are subjected to dry distillation with lime.

(7) The synthesis of the higher phenols by introduction of alkyls into the benzene nucleus takes place readily on heating the phenols with alcohols and ZnCl₂ to 200° (B. 14, 1842; 17, 669; 27, 1614; 28, 407):

$$C_6H_6$$
. OH + (CH₂)₂CH . CH₂ . OH = (CH₃)₃CH[4]C₆H₄[1]OH.

Alkyl ethers of the phenols are simultaneously produced; methyl alcohol yields methyl-phenol C₆H₆.O.CH₂. Magnesium chloride (B. 16, 792) and primary alkali sulphates (B. 16, 2541) possess the same condensing power as ZnCl₂.

(8) Phenols, under the influence of concentrated sulphuric acid, take up unsaturated hydrocarbons—e. g., isoamylene—and form alkyl phenols (B. 25, 2649).

Deportment: Replacement of the Hydrogen Atoms.—(1) The character of the phenols, recalling the acids, expresses itself in the ease with which they form salts, particularly with the alkalies. The hydrogen of the hydroxyl group is also readily replaced (2) by alcohol radicals and (3) by acid radicals. (4) The presence of an hydroxyl group in the place of an aromatic hydrogen atom renders more easy the substitution of other hydrogen atoms by chlorine, bromine, and the nitro-group.

(5) The phenols unite with the diazo-compounds, forming azo- and diazo-dyes: oxy-azo-derivatives (p. 155).

(6) Color Reactions of the Phenols.—On adding phenols (mono- or polyhydric) to a solution of KNO₂ (6 per cent.) in concentrated sulphuric acid, intense colorations arise; with common phenol we get first a brown, their green, and finally a royal-blue color (Reaction of Liebermann) (see B. 17, 1875). Dyes are produced in this manner; their character is as yet unexplained. They have been called dichroines (B. 21, 249).

The phenols afford similar colors in the presence of sulphuric acid, with diazo-compounds, and nitroso-derivatives. Ferric chloride imparts color to the solutions of most phenols. Mercury nitrate, containing nitrous acid, colors nearly all the phenols red (reaction of Plugge) (B. 23, R. 202).

Replacement of the Hydroxyl Group.—(7) When heated with zinc

dust the phenols are reduced to hydrocarbons.

(8) The oxygen of the simple phenols is not very easily replaced by chlorine when phosphorus pentachloride acts upon them. Phenol itself has given the body, C₆H₅OPCl₄ (p. 147). The pentachloride acts with greater ease upon the nitrophenols, forming nitro-chlorbenzenes.

(9) Phosphorus sulphide converts the phenols into thio-phenols.

(10a) The anilines result on heating with zinc ammonium chloride (compare p. 72).
(10b) In the alcohol-ethers of the nitro-phenols (as with the acid esters) we can replace the OH by NH₂, on heating with alcoholic ammonia.

(II) For the oxidation of the alkyl residues of homologous phenols see p. 143.

Nucleus-syntheses.—(1) Compare methods 7 and 8 (p. 141), upon the replacement of the aromatic hydrogen atoms of the phenols by alkyl groups.

(2) The alkali salts of the phenols are converted by carbon dioxide, at higher temperatures, into the alkali salts of oxy-acids—phenol carboxylic

acids (compare salicylic acid).

(3) The phenols also yield phenol carboxylic acids with carbon tetra-

chloride and sodium hydroxide.

- (4) Oxyaldehydes or phenol aldehydes (see salicylaldehyde) are produced from phenols, chloroform (1, 235), and caustic soda.
- (5) The phenols condense with formaldehyde to phenol alcohols (see saligenine). (6) Coumarines (see these) are formed on heating phenols with malic acid and sulphuric acid. (7) Dyestuffs belonging to the aurine series, and derived from triphenylmethane, $\mathrm{CII}(\mathrm{C_6II_5})_3$ (see this), are obtained from the phenols by their action upon benzotrichloride, $\mathrm{C_6II_5}$. (8) The so-called phthaleins are combinations of phthalic acid and o-sulphobenzoic anhydride with the phenols.

Breaking-down of the Benzene Nucleus of the Phenols (pp. 44, 45).

(1) By oxidation of phenol (see this).

(2) By treating the phenols with chlorine, and then decomposing the

chlorine addition products with alkalies.

Benzophenol, Phenol, Carbolic Acid, C₆H₅. OH, melts at 43° and boils at 183°; its specific gravity is 1.084 (0°). It is obtained from amidobenzene, from benzene-sulphonic acid, from the three oxy-benzoic acids, etc., by the methods previously described. It occurs already formed in Castoreum and in the urine of the herbivoræ.

Commercial phenol is a colorless, crystalline mass, which gradually acquires a reddish color on exposure to the air (B. 27, R. 790). Pure phenol crystallizes in long, colorless prisms. It possesses a characteristic odor, burning taste, and poisonous and antiseptic properties. It dissolves in 15 parts water at 20°, and very readily in alcohol, ether, and glacial acetic acid. It is volatile with steam. Ferric salts impart a violet color to its neutral solutions. Bromine water precipitates [2,4,6]-tri-bromphenol from even very dilute solutions.

Diphenols, C₁₂H₈(OH)₂, derivatives of diphenyl (see this), are produced on fusing

phenol with caustic potash.

Diphenylene oxide is produced when phenol is distilled over lead oxide. Aurine results when it is heated with oxalic or formic acid and dehydrating agents (see this). Potassium permanganate oxidizes phenol to inactive or mesotartaric acid (vol. 1). Chlorine finally changes phenol to keto-chlorides, which are derived from di- and tetrahydrobenzene (B. 27, 537). Chlorine and caustic soda convert phenol into trichlor-R-pentene dioxycarboxylic acid (p. 27). The most important reactions of phenol have been previously described.

History.—Runge discovered (1834) phenol in coal tar and called it carbon-oil acid, or carbolic acid. He also observed the physiological properties it possessed in common with creosote. Laurent, in 1841, first obtained it pure and gave it the names hydrate de phényle or acide phénique, from paiveir, to illuminate, probably because it occurs in the tar produced in the manufacture of illuminating gas. Gerhardt, who prepared it from salicylic acid, introduced the name phenol, indicating thereby that it was an alcohol. In 1867 Lister, of Glasgow, showed its great importance in surgery as a disinfectant.

Phenolates.—Phenates, Potassium Phenate, C.H.OK, and Sodium Phenate, C₆H₆ONa, are obtained by dissolving phenol in caustic potash or soda, evaporating the solution and sharply drying the residue. Both salts dissolve readily in water (B. 26, R. 150). Carbon dioxide sets phenol free from them; it is, therefore, not soluble in the alkali carbonates.

Calcium Phenate, (C₆H₅O)₂Ca, and Mercury Phenate, (C₆H₅O)₂Hg. (See B. 20, R. 178, for the compounds of the phenols with aluminium

chloride.)

Homologous Phenols.—It is strange that the cresols, as well as other higher phenols, can not be oxidized by the chromic acid mixture; the OH-group prevents the oxidation of the alkyl groups by chromic acid. If, however, the phenol hydrogen is replaced by alkyls or acid radicals (in the phenol ethers and esters), then the oxidation of the alkyl does take place with the production of ether acids or ester acids.

The readily prepared sulphuric or phosphoric acid esters of the homologous phenols are best adapted for oxidation with an alkaline permanganate solution (B. 19, 3304), whereas the free phenols are completely

destroyed by this reagent (compare oxidation of phenol, above).

The oxidation of the alkyls in the sulpho-acids of the homologous phenols is similarly influenced by the sulpho-group. In general negative atoms or groups prevent the oxidation of alkyls in the ortho-position by acid oxidants, whereas alkaline oxidants—e.g., KMnO —do precisely the reverse in that they first oxidize the alkyl group holding the ortho-position (A. 220, 16). The methyl groups of the methyl phenols, such as the cresols and xylenols, are converted by molten alkalies into carboxyl groups, and there result oxybenzoic acids, oxytoluic acids, oxyphthalic acids, etc. (compare the like behavior of the homologous pyrrols and indols).

Other rearrangement reactions are given on p. 142. The liquid homologous phenols are particularly characterized by the melting points of their benzoyl esters; therefore

these will be given in connection with the various members.

I. Cresols, Oxytoluenes, CH₃. C₂H₄OH.—The three isomerides occur in coal-tar

and beech-wood tar.

They are obtained from the toluidines by method I, and from the toluene-sulphonic acids by method 2 (p. 141). They have a similar odor, but it is more disagreeable than that of phenol. They are less poisonous, and are disinfectants. They are changed to toluene when heated with zinc dust. Sodium and carbon dioxide produce the corresponding cresotinic acids.

See above for their behavior toward molten caustic potash and other oxidizing

agents. o-Cresol is obtained from carvacrol (p. 145) and the m-body from thymol (see below). The latter is also prepared from the dibromide of synthetic β -methylketo-Rhexene (see this) by the elimination of hydrogen bromide (A. 281, 98).

Ferric chloride colors o-cresol blue. The crude cresols are used as disinfectants: creolin is a solution of the crude cresols in alkalies; cresolin is a solution of the same in resin soaps, while lysene or lysol is a solution of crude cresols in olive soaps. See B. 14, 687, for the behavior of the cresols in the animal organism.

687, for the behavior of the cresols in the animal organism.

2. Phenols, C_8H_9OH .—Oxydimethyl benzenes and oxyethyl benzenes. The six possible xylenols, $C_6H_4(C_1H_3)_2$. OH, have been prepared.

Ethyl Phenols, $C_6H_4(C_2H_3)$. OH.—From the ethyl-benzene-sulphonic acids (B. 27, R. 189). The ortho-compound is a liquid, boiling at 203°; its benzoyl derivative melts at 39°. The meta boils at 214°; its benzoyl derivative melts at 52°. The para is a solid, melts at 45°, and boils at 215°; its benzoyl compound melts at 59°.

3. Phenols, C_9H_{11} . OH.—Mesitol, $C_9H_3(CH_3)_3$. OH, from amido-mesitylene and mesitylene-sulphonic acid, melts at 68° and boils at 220°. [1]OH[2,4,5]-Pseudocumenol, $C_8H_2(CH_3)_3$. OH, from pseudocumene-sulphonic acid, melts at 73° and boils at 232° (B. 17. 2076).

(B. 17, 2976).

m-n-Propyl Phenol, from isosafrol, melts at 26° and boils at 228° (B. 23, 1162). p-n-Propyl Phenol boils at 232°. p-Isopropyl Phenol melts at 61° and boils at 229°. It is also produced along with hydroquinone (p. 162) on decomposing diphenol-3-propane, (CH₃)₂C(C₆H₄OH)₂ (from the action of fuming hydrochloric acid on accetone and wheel with meltan causity protects (B. 28, P. 234). and phenol), with molten caustic potash (B. 25, R. 334).

4. Phenols, C₁₀H₁₃. OH.—There are twenty possible isomerides. Thymol and carvacrol merit notice. They occur in vegetable oils. Both are derivatives of ordinary p-cymene (p. 56), and contain the isopropyl group.

Thymol, when heated with P₂O₅, breaks down into propylene and m-cresol, while carvacrol, under similar treatment, yields propylene and

o-cresol.

Thymol, = [3]-Methyl-[6]-isopropyl phenol,
$$C_3H_7[6]C_6H_3$$
 { [1]OH 3 | Carvacrol, = [2]-Methyl-[5]-isopropyl phenol, $C_3H_7[5]C_6H_3$ { [1]OH 2 | CH₃

Thymol, melting at 44° and boiling at 230°, crystallizes in large, colorless plates. It exists with cymene, C₁₀H₁₄, and thymene, C₁₆H₁₆, in oil of thyme (from Thymus vulgaris), and in the oils of Ptychotis ajowan and Monarda punctata. To obtain the thymol shake these oils with potassium hydroxide, and from the filtered solution precipitate thymol with hydrochloric acid. It is artificially prepared from nitrocuminaldehyde (see this), as well as from dibrom-menthone, by the splitting-off of hydrogen bromide (B. 29, 420). It has a thyme-like odor and answers as an antiseptic.

Ordinary cymene is obtained by distilling it with P2S5. Thymoquinone (see this) is

produced in its oxidation.

Iodine and caustic potash convert thymol into di-iodthymol, a diphenyl derivative which has been substituted for iodoform under the names aristol and annidalin. Compare: Die Arzneimittel der organischen Chemie von Thoms.

Carvacrol, Cymophenol, melting at oo and boiling at 236°, isomeric with thymol, occurs already formed in the oil of certain varieties of satureja, also in Briganum hirtum, and is obtained from an isomeric carvol, a dihydrocymene derivative (see this) contained in the oil of Carvum carvi, and certain other oils, when it is heated with glacial phosphoric acid (B. 19, 12). It is further prepared by heating with iodine (part), using a return condenser. It is made artificially from cymene-sulphonic acid (B. 11, 1060).

Distilled with P₂S_a it yields cymene and thiocymene, cymothiophenol, C₁₀H₁₂. SH, boiling at 235°.

s-Garvacrol, (CH₃)[3](CH₃)₂CII[5]C₆H₃[1]OH, melts at 54° and boils at 241° (B. 27, 2347). Methyl-p-norm.-propyl phenol, (CH₃)[2]C₃H₇[5]C₆H₃OII, from the corresponding sulpho-acid, boils at 240° (B. 29, R. 417). p. Tertiary Butyl Phenol, (CH₃)₂C[4]C₆H₄[1]OII, melting at 98° and boiling at 237°, in the internal control of the control of t

is obtained from isobutyl alcohol, phenol, and zinc chloride (B. 24, 2974).

p. Tertiary Amyl Phenol, (CH₃)₄(C₂H₅)C[4](C₄H₄[1]Ol1, melting at 93° and boiling at 266°, results from the action of ZnCl₂ upon isoamyl alcohol or tertiary amyl alcohol, and from isoamylene, phenol, acetic acid, and sulphuric acid (B. 28, 407).

Diethyl Phenols (B. 22, 317).

Tetramethyl Phenols (B. 15, 1854; 17, 1916; 18, 2842; 21, 645, 907).

Pentamethyl Phenol melts at 125° and boils at 267° (B. 18, 1826).

DERIVATIVES OF THE MONOHYDRIC PHENOLS.

The behavior of the phenols was given under the example selected—ordinary phenol. Because this can be obtained with comparative ease, more derivatives of it, than of its homologues, have been prepared. the following pages the derivatives of the homologues will only be brought forward and discussed in case they possess theoretical or practical value, and then in connection with the compounds of the corresponding phenol.

Phenol Alcohol-ethers.—(1) Like the ethers of the aliphatic alcohols (1, 132), they result from the interaction of alkyl iodides and phenates. The phenol is digested with caustic potash and the alkyl iodide or methyl chloride is conducted over sodium phenate heated to 200° (B. 16, 2513).

- (2) By heating a mixture of the alkali salts of the phenols with an excess of alkyl sulphates, in aqueous or alcoholic solution (B. 19, R. 139).
 - (3) Upon heating the benzene-sulphonic esters with phenols (B. 27, R. 955).
 (4) Together with hydrocarbons on decomposing benzene diazo compounds with alco-

hols (B. 25, 1973) (p. 104).

(5) By the dry distillation of the phenol ethers of the oxy-acids with lime or baryta:

CO₂H[1]. C₆H₄[4]OCH₃
$$\xrightarrow{\text{-CO2}}$$
 \Rightarrow C₆H₅OCH₃ Anisol.

(6) The phenols are converted at the ordinary temperature by diazomethane, with evolution of nitrogen, into their methyl ethers (B. 28, 857):

 $C_aH_aOH + CH_aN_a = C_aH_aOCH_a + N_a$

Boiling alkalies do not alter the alcohol ethers. When, however, they are heated with hydriodic or hydrochloric acid, they split up into their components:

 C_aH_a . O. $CH_a + HI = C_aH_a$. OH + CH_aI .

Al₂Cl₆ also decomposes them (B. 25, 3531). They behave like the aromatic hydrocarbons with Cl, Br, I, NO₂H, and SO₄H₂.

Anisol, Methyl Phenyl Ether, C_0H_δ . O. CH_{η} , is produced by distilling anisic or p-methyl salicylic acid. It boils at 152°; its specific gravity at 15° is 0.991. It is not reduced by zinc dust.

Phenetol, Ethyl Phenyl Ether, (C₈H₅). O. C₂H₅, boils at 172°, and has the specific gravity 0.9822 (0°). The *isoamyl ether* boils at 225°.

Bromethyl Phenyl Ether, BrCH₂. CH₂. O. C₈H₅, melts at 39° (J. pr. Ch. [2] 24,

242). Phenol-ethylene Ether, Glycol-diphenyl Ether, CaH5OCH2. CH2OCaH5, melts at 95°. Glycol-monophenyl Ether boils at 165° (80 mm.) (B. 29, R. 289). Phenyl Glycrol Ether (B. 24, 2146).

Phenoxalkylamines (1, 311).—β-Phenoxethylamine, NH₂. CH₂. CH₂. O. C₄H₅, boils at 228° (B. 24, 189). γ-Phenoxypropylamine, NH₂. CH₂. CH₃. CH₄. O. C₄H₅, boils at 241° (B. 24, 2637). [δ-Amidobutylphenyl Ether] NH₂CH₂CH₃. CH₄. CH₄. CH₄OC₄H₅, boils at 225° (B. 24, 3232).

Phenol ethers of aldehyde alcohols, ketone alcohols, and alcohol acids have been obtained from the corresponding chlorinated aldehydes, ketones, and carboxylic acids by the action of sodium phenate:

Phenoxyacetaldehyde, C₆H₅O. CH₂. CHO, boils at 119° (30 mm.) (B. 28, R. 295). Phenoxyacetone, Phenacetol, C₆H₅O. CH₂. CO. CH₃, boiling at 230°, is condensed by concentrated sulphuric acid to methyl cumarone (see this) (B. 28, 1253). Phenoxyacetic Acid, C₆H₅O. CH₂. COOH, melting at 96°, is isomeric with mandelic acid, C₆H₅CH(OH). COOH. It results from monochloracetic acid and potassium phenate at 150°, as well as by the oxidation of phenoxyacetaldehyde. It is a strong antiseptic (B. 19, 1296; 27, 2796). Diphenoxyacetic Acid, (C₈H₆O)₅CHCO₅H, melts at 91° (B. 27, 2796). a and \(\gamma\)-Phenoxybutyric Acid melt at 99° and 60° (B. 29, 1421). a-Phenoxyacetoacetic Ester, CH₃. CO. CH(OC₆H₆)CO₂C₂H₆, from sodium phenate and a-chloracetoacetic ester, is a thick oil. Concentrated sulphuric acid condenses it to methyl. cumarilic ester.

Phenol Ethers.—Phenyl Ether, (C₆H₅)₂O, Diphenyl Oxide, melting at 28° and boiling at 252°, is produced by distilling copper benzoate (together with benzoic phenyl ether) and digesting diazobenzene sulphate with phenol (B. 25, 1973); also by heating phenol with zinc chloride to 350°, or, better, with aluminium chloride (B. 14, 189). It crystallizes in long needles, and possesses an odor resembling that of geraniums. It dissolves readily in alcohol and ether. It is not reduced on heating with zinc dust or hydriodic acid.

Nitrated phenyl ethers have been obtained by the interaction of the corresponding nitrohaloid benzenes and the potassium salts of phenols: o-Nitrophenyl Ether, $C_6H_5O \cdot C_6H_4NO_2$, boils at 235° (60 mm.). o, o'-Dinitrophenol Ether, (NO₂ · C₆H₄)₂O, melts at 114° (B. 29, 1880, 2084).

Acid Esters of Phenol.—The acid esters are obtained by acting with acid chlorides or anhydrides upon the phenols or their salts; also by digesting the phenols with acids and POCl₂. To effect the substitution of all the hydroxyl-hydrogen atoms in the polyhydric phenols by acetyl groups, it is recommended to heat them with acetic anhydride and sodium acetate. On boiling with alkalies, or even with water, they, like all esters, break down into their components.

Esters of Inorganic Acids.—Phenyl Sulphonic Ester is not known in

a free state. Its sodium salt, NaSO₂OC₆H₆, results from the action of SO₂ upon sodium phenate. Methyl iodide converts it into methyl sulphonic phenyl ester, CH₃SO₂OC₆H₅ (compare B. 25, 1875).

Phenylsulphuric Acid, CaHa. O. SOaH, is not known in a free state; when liberated from its salts by concentrated hydrochloric acid, it immediately breaks down into phenol and sulphuric acid. Its potassium salt, C_0H_0 . O. SO_3K , forms leaflets, not very soluble in cold water, and occurs in the urine of herbivorous animals, and also in that of man and the dog after the ingestion of phenol. It is synthetically prepared, like other phenols, on heating potassium phenoxide with an aqueous solution of potassium pyrosulphate (Baumann, 9, 1715).

The phenyl sulphuric acids are very stable in aqueous and alkaline solution; upon digesting with mineral acids, however, they are very rapidly decomposed. When potassium phenylsulphate is heated in a tube, it passes quietly into potassium p-phenol-sul-

phonate.

Phenyl Esters of the Phosphoric Acids.—These arise in the action of PCl, and POCl, (A. 239, 310; 253, 120):

Phenylphosphorous Chloride, .				. CaHaO	. PCl.,	boils at	90° (11 mm.)
Diphenylphosphorous Chloride,				. (Č,H,(O),PCĪ,	66	1720	" '
Triphenylphosphite,						**	220°	"
Phenylphosphoric Chloride, .						"	1210	"
Diphenylphosphoric Chloride,				. (C.H.(oi.Poci.	"	1950 (14 mm.)
Triphenylphosphate, m. p. 45°,				. (C,H,(O), PO,	66	245° (ı i mm.
(B. 18, 1700).				, 6 5	/6 - /		.5 (,

The two phenylphosphorous chlorides take up chlorine:

Diphenylphosphoric Trichloride, (C₆H₅O)₂PCl₃

Phenyl Silicates (B. 18, 1679).

Phenyl Esters of Monocarboxylic Acids.—Phenyl Formate (J. pr. Ch. [2] 31, 467). Phenyl-ortho-formic-ester, CH(O.C₆H₅)₃, is formed by boiling phenol with sodium hydroxide and chloroform. It melts at 71° and distils at 265°, under 50 mm. pressure (B. 18, 2656).

Phenyl Acetate, CH₂. COOC₆H₆, boils at 195° (B. 18, 1716). Orthoacetic Phenyl Ester, CH₂C(OC₆H₆)₃, melts at 98° (B. 24, 3678).

Phenyl Carbonates.—The free phenyl-carbonic acid is not known. The opposite is true of Sodium Phenyl Carbonate, CaHgOCO, Na. It is produced when CO, acts upon sodium phenoxide (under pressure).

It is a white hygroscopic powder, decomposed again by water. When heated under pressure to 120-130°, sodium salicylate, HOC₂H₂CO₃Na, results, just as phenolsulphonic acid is obtained from phenylsulphuric acid (see above). When heated to 190° with

sodium phenate, sodium phenyl carbonate yields disodium salicylate and phenol.

Phenyl Carbonate.—The carbonic acid ester, CO(O. C₆H₆)₂, is produced on heating phenol and phosgene gas, COCl₂, to 150°. It is readily obtained by leading phosgene gas into the aqueous solution of sodium phenylate (J. pr. Ch. 17, 139; B. 17, 287). It crystallizes from alcohol in shining needles, and melts at 78°. It yields sodium salicylate (see this) when heated to 200° with sodium hydroxide. Urea results if it be heated with

ammonia (B. 23, 694).

Mixed carbonates containing phenol and alkyls—e. g., phenyl-ethyl carbonate, CO₃(C₃H₅)(C₆H₅)—are produced by the action of chlorformic esters upon the sodium salts of the phenois.

Diphenylthiocarbonic Ester, $C_aH_6OCSOC_aH_5$ (B. 27, 3410). Phenyl Carbaninau, $NH_1COOC_aH_5$, melts at 1418 (A. 244, 43). Phenylcarbanic Phenyl Ester, $C_aH_6NHCO_2C_aH_6$, from carbanile (p. 89) and phenol, melts at 1240 (B. 18, 875;

27, 1370).

27, 1370).

Phenylthiocarbamic Phenyl Ester, C₆H₆O. CSNHC₈H₆, melting at 148°, is produced on heating phenyl mustard oil with phenol to 280° (B. 29, R. 177). Phenylimidocarbonic Phenyl Ester, C₈H₆N: C(OC₈H₅)₃, melting at 136°, is obtained from isocyan-phenyl chloride (p. 89) and sodium phenate (B. 28, 977).

Phenyl-allophanic Ester, CO
NH₂
NH₂ CO₂, C₄H₅, is produced by conducting cyanic acid

vapors into anhydrous phenol. A crystalline mass.

Phenyl Esters of Divarboxylic Acids.—Phenyl Oxalic Ester, (COOC₈H₈)₁₀, melts with decomposition at 130° (J. pr. Ch. [2] 25, 282). Ethyl Phenyl Oxalic Ester, COOC₁-H₈. COOC₆H₅, boiling at 236°, is obtained from ethyl oxalic chloride (vol. 1). The succinic ester melts at 118° and boils at 330°. Phenyl Firmaric Ester, melting at 161°, decomposes when distilled slowly into CO₂, phenyl cinnamic ester (see this) and stilbene (see this) (B. 18, 1948).

PHENOL SUBSTITUTION PRODUCTS.

Phenol Haloids. — Formation. (1) Chlorine and bromine react readily with phenols; this is exemplified in bromine precipitating phenol quantitatively from its aqueous solutions as [10H,2,4,6]-tribromphenol. Chlorine and bromine enter the ortho- and para-positions; there result at first the [1,2]- and [1,4]-mono-, then the [1,2,4]-di-, and finally the [1,2,4,6]-trisubstitution products. At 150-180°, by action of chlorine or bromine vapors, abundant quantities of o-chlor- and o-bromphenol (B. 27, R. 957) are produced.

The iod-derivatives are formed by adding iodine and iodic acid to a

dilute potassium hydroxide solution of phenol:

$$5C_6H_5OH + 2I_2 + IO_3H = 5C_6H_4IOH + 3H_2O_4$$

or by the action of iodine and mercuric oxide. Di-iod-phenol is the chief production in the latter case.

(2) From substituted anilines by the replacement of NH, by OH, which may be brought about by the diazo compounds; this reaction leads to pure mono-haloid phenols. (3) From the nitrophenols by replacing the nitro-group with halogens (effected through the amido- and diazo-derivatives). (4) By distilling substituted oxyacids with lime or baryta.

Deportment.—(1) The introduction of halogen atoms considerably increases the acid character of phenol; thus, trichlorphenol readily decomposes the alkaline carbonates. (2) When fused with potassium hydroxide, the halogen is replaced by the hydroxyl group (p. 141).

In this reaction it frequently occurs, especially at high temperatures, that not the corresponding isomerides, but rather the more stable derivative results; for example, all the bromphenols yield resorcinol. The caustic potash fusion is, therefore, not applicable in determining constitution.

(3) Sodium amalgam causes the replacement of the halogen atoms by hydrogen.

Monohaloid Phenols.—The monochlorphenols in particular are characterized by a disagreeable, very adherent odor. The brom- and iod-phenols being attacked at a lower temperature than the chlor-derivatives, are changed on fusing with potash into the corresponding dioxybenzenes. The higher the temperature rises in the fusion of the o- and p-compounds, the greater will be the yield of resorcinol or m-dioxybenzene; the three isomeric monochlorphenols yield resorcinol:

	Ortho-		Me	ta-	Pa	ra-
Chlorphenol, Bromphenol, Iodphenol,	M. P. 7°	B. P. 176° 195°	M. P. 28° 32° 40°	B. P. 212° 236°	M. P. 41° 66° 94°	B. P. 217° 238° — (B. 20, 3019).

See B. 29, 997, 1409, 2595, for the iodanisols and phenetols.

Polyhaloid Phenols.—In the direct substitution the [2,4]-di- and [2,4,6,]-trihaloids are produced quite readily:

		M. P.	B. P.		M. P.	B. P.
-	[2,4]-Dichlorphenol,	· 43°	210°	[2,4,6]-Trichlorphenol,	68°	244°
	2,4 Dibromphenol,	40°	_	[2,4,6] Tribromphenol,	92°	
Ì	[2,4] Di-iodphenol,	72°	_	[2,4,6]-Tri-iodphenol,	156°	_

M. P. M. P. M. P. Pentachlorphenol, 186° (B. 27, 549). [2,3,4,6]-Tetrabromphenol, 120° (A.137, 209). Pentabromphenol, 225°.

The tri-, tetra-, and penta-chlor- and -bromphenols take up chlorine and bromine, becoming chlorinated and brominated oxodi- and oxotetrahydrobenzenes (see also B. 28, R. 1012). 2,4,5-Pseudocumenol yields, when brominated under suitable conditions, a tribrompseudo-cumenol, insoluble in alkali. It is distinguished by the great reactivity of one of its bromine atoms. Its peculiar behavior renders it very probable that it is really a derivative of keto-dihydrobenzene (B. 29, 2329; 30, 744, 753). 2,5-Xylenol yields a very similar tribrom-derivative (B. 29, 2348).

NITROPHENOLS.

The phenols, like the anilines, are very readily nitrated. The entrance of the nitro-groups increases their acid character very considerably. All nitrophenols decompose alkaline carbonates. Trinitrophenol is a perfect acid in its behavior; its chloranhydride, $C_6H_2(NO_2)_3Cl$, reacts quite readily with water, re-forming trinitrophenol (p. 68). The benzene nucleus of the nitrophenols is capable of ready substitution with the halogens; whereas the nitrohydrocarbons are chlorinated with difficulty.

The nitro-groups replace the o- and p-hydrogen atoms referred to hydroxyl, and with reference to one another in the m-position:

$$C_{e}H_{b}OH \xrightarrow{C_{e}H_{4}} \left\{ \begin{bmatrix} 1 \end{bmatrix}OH \\ 2 \end{bmatrix}NO_{2} \\ \longrightarrow C_{e}H_{4} \left\{ \begin{bmatrix} 1 \end{bmatrix}OH \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \left\{ \begin{bmatrix} 1 \end{bmatrix}OH \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \left\{ \begin{bmatrix} 1 \end{bmatrix}OH \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \left\{ \begin{bmatrix} 1 \end{bmatrix}OH \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \left\{ \begin{bmatrix} 1 \end{bmatrix}OH \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \left\{ \begin{bmatrix} 1 \end{bmatrix}OH \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O_{e}H_{4} \right\} \left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}NO_{2} \\ O$$

Mononitrophenols, NO₁. C_4H_4 . OH.—Dilute nitric acid converts phenol into o- and p-mononitrophenol (in the cold it is chiefly the p-compound which is formed). At -67° , with use of the electric spark, there is five times as much of the p-body as at -40° (B. 26, R. 362). The o- and p-compounds are separated by distillation with steam, in which the

latter is not volatile. Phenol in presence of sulphuric acid is also nitrated by nitrogen dioxide (B. 24, R. 722).

o- and p-Nitrophenols are obtained by heating the corresponding chlor- and bromnitrobenzenes with caustic potash to 120°, whereas m-brom-nitrobenzene does not react under similar circumstances (p. 67). Ortho- and para-nitrophenols are likewise produced from the corresponding nitranilines by heating with alkalies (p. 93). m-Nitrophenol is formed from m-nitraniline (from ordinary dinitrobenzene) by boiling the diazocompound with water. p-Nitrophenol has also been obtained synthetically from nitromalonic aldehyde with acetone.

o-Nitrophenol melts at 45° and boils at 214°; its methyl ether melts at + 9° and boils

at 265°.

m-Nitrophenol melts at 96°; its methyl ether melts at 38° and boils at 254°.
p-Nitrophenol melts at 114°; its methyl ether melts at 48° and boils at 260°.

o- and m-Nitrophenols form yellow crystals; the latter is rather soluble in water. The o-body has a peculiar odor and sweet taste. Its sodium salt forms dark-red prisms. p-Nitrophenol crystallizes from hot water in long, colorless needles. The potassium salt crystallizes in yellow needles with two molecules of water.

Bromine converts p-nitrophenol into dibrom-p-nitrophenol (1,4,2,6,OH in 1), melt-

ing at 141°.

PCl₅ converts o- and p-nitrophenols into o- and p-chlornitrobenzenes (p. 67).

Dinitrophenols, $(NO_2)_2C_4H_3OH.$ —a- or [1OH, 2,4]-Dinitrophenol, melting at 114° , and β - or [1OH, 2,6]-Dinitrophenol, melting at 64° , are produced in the nitration of phenol and of o-nitrophenol. The a-compound can also be obtained from p-nitrophenol, as well as from m-dinitrophenole, by means of alkaline potassium ferricyanide. The a-methyl ether melts at 86° . It is transformed into $[1NH_2, 2,4]$ -dinitraniline by heating with ammonia.

The nitration of [1,3]-nitrophenol produces three isomeric dinitrophenols, melting at 104°, 134°, and 141°. Further nitration produces trinitrophenols and trinitroresorcinol

(p. 161).

Trinitrophenols.—Picric Acid, $C_0H_1(NO_1)_3$. OH, melting at 122°, is obtained by the nitration of phenol, of [1,2]- and [1,4]-nitrophenol, and of the two dinitrophenols; also, by the oxidation of symmetrical trinitrobenzene with potassium ferricyanide. Its structure is therefore 1,2,4,6 (OH in 1).

Picric acid is produced in the action of concentrated nitric acid upon various organic substances, like indigo, aniline, resins, silk, leather, and

wool

History.—Welter, in 1799, first prepared pure picric acid by nitrating silk. It was named Welter's bitter. Liebig called it carbon-nitric acid, carbasotic acid. Dumas analyzed it and called it picric acid, from πικρός, bitter. Laurent, in 1842, discovered it to be a derivative of phenol.

Properties.—Picric acid crystallizes from hot water and alcohol in yellow leaflets or prisms which possess a very bitter taste. It dissolves in 160 parts of cold water and rather readily in hot water. Its solution imparts a beautiful yellow color to silk and wool. It sublimes undecomposed when carefully heated.

Deportment.—With many hydrocarbons, like benzene, naphthalene, and anthracene, picric acid forms beautiful, crystalline derivatives, well adapted for the recognition and separation of the higher aromatic hydro-

carbons

Phosphorus pentachloride converts picric acid into trinitro-chlorbenzene, C₆H₂ (NO₂)₂·Cl (p. 68).

Prussic acid is produced on boiling a solution of barium picrate with baryta water.

Picric acid is converted by potassium cyanide into the potassium salt of isopurpuric or picrocyaminic acid, C₈H₄N₅O₆K. It crystallizes in brown leaflets with green-gold lustre, and formerly appeared in commerce under the name Grénat soluble. It is no longer The free acid is not known.

Salts and Ethers.—The potassium salt, CoH2(NO2)3. OK, crystallizes in yellow needles,

soluble in 260 parts of water at 15°.

The sodium salt is soluble in 10 parts water at 15°, and is separated from its solution by sodium carbonate. The ammonium salt consists of beautiful, large needles, and is applied in explosive mixtures. All the picrates explode very violently when heated or struck. The methyl ester of picric acid is produced in the nitration of anisol. It melts at 65°.

The ethyl ester melts at 78°.

β-Trinitrophenol, melting at 96°, and γ-Trinitrophenol, melting at 117°, have been obtained from the dinitrophenols resulting from the nitration of m-nitrophenol.

Tetranitrophenol, melting at 130°, consists of golden yellow needles. It is produced in the oxidation of diquinoyltrioxime (see this). It is very explosive (B. 30, 184).

Nitrocresols.—o- and p-Cresol are easily converted into dintro-derivatives (B. 15, 1864; 17, 270). The [2,6]-dinitro-p-cresol, melting at 84°, has been introduced into trade in the form of its sodium salt, bearing the name Victoria orange, or Safran surrogate. It is an orange-yellow dye. It is not extensively applied as yet. When m-cresol is nitrated, it yields a trinitrocresol, (NO₂)₃C₆H(CH₃)OH, melting at 106°. This has also been formed from nitrococcic acid (see this).

Haloid Nitrophenols.—Numerous representatives of this class have been obtained by the action of the halogens upon the nitrophenols or by the nitration of the haloid

phenols.

It is interesting to note that p-*Nitro*-o-iodanisol, C₀H₃[4]NO₂[2]I[1]OCH₂, has en prepared both in the nitration of o- as well as in that of p-iodanisol. In the latter been prepared both in the nitration of o- as well as in that of p-iodanisol. case, therefore, a migration or wandering of the iodine atom in the nucleus has occurred (B. 29, 997).

NITROSO-COMPOUNDS OF THE PHENOLS.

The nitroso-phenols are made: (1) by the action of nitrous acid upon phenols (Baeyer, B. 7, 964), when the monohydric phenols yield only mononitroso-compounds; whereas dinitroso-derivatives are obtained from the dihydric meta-dioxybenzenes, like resorcinol.

- (a) Nitrous acid, from alkali nitrite and dilute sulphuric acid or acetic acid, is allowed to act upon the phenols (B. 7, 967; 8, 614); (b) by means of the nitrites of heavy metals, which are decomposed by the phenols themselves (B. 16, 3080); (c) from nitrosyl sulphuric acid, HO.SO₂. NO, and phenols (A. 188, 353; B. 21, 429); (d) from amyl nitrite and sodium phenolates (B. 17, 803).
- (2) Upon boiling p-nitroso-alkylamines, like nitroso-dimethylaniline (1, 163; 11, 94) with alkalies:

$$NO[4]C_aH_4[1]N(CH_2)_2 + NaOH = NO[4]C_aH_4[1]OK + HN(CH_2)_2.$$

(3) By the action of HCl-hydroxylamine upon quinones in aqueous or alcoholic solution. Free hydroxylamine reduces the quinones to hydroquinones (B. 17, 2061). This method favors the idea that the nitrosophenols are quinone monoximes (Goldschmidt, B. 17, 801). Hence, three constitutional formulas have been brought forward for p-nitrosophenol or quinone monoxime (Quinones, see these):

p-Nitrosophenol, Quinoxime, crystallizes from hot water in colorless, delicate needles, which readily brown on exposure, and from ether it separates in large, greenish-brown leaflets. It is soluble in water, alcohol, and ether, and imparts to them a bright green color. heated, it melts with decomposition, and deflagrates at 110-120°. sodium salt crystallizes in red needles, containing two molecules of water of crystallization.

The methods of producing nitrosophenol from phenol with nitrous acid, and from nitroso-dialkyl anilines, argue for the nitroso-formula of the nitrosophenols; as does their oxidation to p-nitrophenol with nitric acid or with an alkaline potassium ferricyanide solution.

The quinoxime formula is supported by their formation from quinone with hydroxylamine hydrochloride and the conversion into quinodioxime, as well as by the formation of hypochlorous esters, C₆H₄(O). NOCl, when acted upon by bleaching lime (B. 19, 280). Further, the behavior of the related nitrosonaphthols (see these), and finally the feeble basic character of the nitrosophenols (B. 18, 3198). The reduction to p-amidophenol is in harmony with both formulas.

The nitrosophenols can be changed to nitrosoanilines (p. 94). Hydrochloric acid converts nitrosophenol into dichloramido-phenol. With nitrous acid and with hydroxyl-

amine it yields p-diazophenol:

$$C_6H_4(OH)NO + NH_9.OH = C_6H_4(OH).N_9.OH + H_9O.$$

In a similar manner it forms azo-compounds with the amines (p. 155). Phenylhydrazine reduces it very readily to amidophenol (B. 29, R. 294). On adding a little concentrated sulphuric acid to a mixture of nitrosophenol and phenol, we obtain a dark red coloration, which changes to dark blue upon adding caustic potash (p. 141).

Quinon-dioxime will be described together with quinone (see this). "Nitroso-o-cresol, from o-cresol and toluquinone (see this) (B. 21, 729), melts at 134°. Nitrosothymol melts

at 160° (B. 17, 2061).

AMIDOPHENOLS.

They result from the reduction of nitrophenols, and amidophenolderivatives, in a similar manner, from the corresponding nitrophenolderivatives. In the case of the poly-nitrated phenols, ammonium sulphide occasions but a partial, tin and hydrochloric acid, however, a complete, reduction of the nitro-groups (p. 71). For special methods of formation, see m- and p-Amidophenol.

Deportment.—The free amidophenols decompose quite easily, especially

in moist air on exposure to light.

The amido-group considerably diminishes the acid character of the phenols. This class of derivatives no longer forms salts with alkalies, and only yields such compounds with the acids.

Like the o-phenylenediamines (p. 96), the o-amidophenols form heterocyclic deriva-These are anhydro-bases, the *benzoxazoles*, corresponding to the see these). The *benzothiazoles* (see these) are similar bodies obtained tives with ease. benzimide azoles (see these). from the o-amidothiophenols.

o-Amidophenol, NII₂[2]C₆H₄[1]OH, melting at 170°, dissolves with difficulty in water. o-Anisidine, NH₂[2]C₆H₄[1]OCH₃, boils at 218°. Oxethyl-o-amidophenol, HOCH₂. CH₂NH[2]C₆H₄[1]OCH₃, boils at 290-310°.

Methylation of the Amido-group of o-Amidophenol (B. 23, 246).—When o-amidophenol (B. 23, 246). phenol in methyl alcohol is treated with methyl iodide and caustic potash, and later with hydrogen iodide, there results the iodide of an ammonium base, which moist silver oxide changes to the ammonium hydroxide. The latter loses water at 105° and changes to a cyclic ammonium derivative similar to betaine: o-Trimethyl-ammonium Phenol, which, heated to higher temperatures, rearranges itself into o-dimethylanisidine. The hydrochloride of the ammonium base breaks down upon distillation into methyl chloride and o-dimethylamidophenol, melting at 45°.

o-Imidodiphenyl Oxide, *Phenoxasine*, O<\(\begin{align*}{c}_{0}^{\text{H}} \display \text{NH}, will be described together with thiodiphenylamine, hydrophenazine and phenazine (p. 96) under the heterocyclic compounds. (Compare also Pyrocatechol, p. 159.)

compounds. (Compare also Pyrocatechol, p. 159.)
o-Oxethylanisidine, HO.CH₁.CH₂.NH[2]C₆H₄[1]OCH₃, from o-anisidine and ethylene chlorhydrin (1, 301) (compare Condensations of the o-Amidophenols), boils at 305°.

o-Oxyphenyl Urea, NH₄CONH[2]C₂H₄[1]OH, melts at 154°. o-Oxyphenylthiurea, NH₄CSNH[2]C₂H₄[1]OH, melts at 161°. (Compare Condensations of the o-Amidophenols.)

The Condensations of the o-Amidophenols.—Like the o-diamines (p. 95) and o-amidothiophenols (p. 157), the o-amidophenols are highly suitable for the formation of o-condensation products:

(1) Bensoxazoles result by the union of o-amidophenol with carboxylic acids; thus, with acetic acid the product is μ-methylbenzoxazole. (2) With phosgene it is μ-oxybenzoxazole, or carbonyl amidophenol. (3) The latter body is also produced upon heating o-oxyphenyl urea (see above), and in like manner (4) o-oxyphenylthiurea yields o-oxyphenyl mustard oil. (5) Nitrous acid converts several substituted o-amidophenol into nather stable diazides; thus, dichlor-o-amidophenol becomes dichlor-o-diazophenol. (6) o-Oxyethylanisidine, when heated with hydrochloric acid, becomes phenmorpholine (see this). (7) Oxidants convert o-amidophenol into oxyphenoxazine (see this). (8) o-Amidophenol and pyrocatechol condense to phenoxazine (see this):

$$C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O H \\ \begin{bmatrix} 2 \end{bmatrix} N H_{5} \end{bmatrix} \right\} C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O \\ \begin{bmatrix} 2 \end{bmatrix} N \right\} C. CH_{8} \quad \mu\text{-Methylbenzene Oxazole Ethenylamidophenol} \\ COCl_{2} \\ C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O \\ \begin{bmatrix} 2 \end{bmatrix} N H \right\} CO \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O \\ \begin{bmatrix} 2 \end{bmatrix} N \right\} C. OH \text{ or Carbon-via mido-phenol} \\ C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O H \\ \begin{bmatrix} 2 \end{bmatrix} N H CONH_{1} \\ \end{bmatrix} C. OH \text{ or Carbon-via mido-phenol} \\ C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O H \\ \begin{bmatrix} 2 \end{bmatrix} N H CSNH_{2} \\ \end{bmatrix} C. OH \text{ or Carbon-via mido-phenol} \\ C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O H \\ \begin{bmatrix} 2 \end{bmatrix} N H CSNH_{2} \\ \end{bmatrix} C. OH \text{ or Oxyphenyl Mustard Oil} \\ C_{6}H_{3}Cl_{2}\left\{ \begin{bmatrix} 1 \end{bmatrix} O H \\ \begin{bmatrix} 2 \end{bmatrix} N H CSH_{2} \\ \end{bmatrix} C. OH \text{ or Oxyphenyl Mustard Oil} \\ C_{6}H_{3}Cl_{2}\left\{ \begin{bmatrix} 1 \end{bmatrix} O H \\ \begin{bmatrix} 2 \end{bmatrix} N H_{2} \\ \end{bmatrix} C. OH \text{ or Oxyphenol} \\ C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O CH_{2} \\ \end{bmatrix} C. OH \text{ or Oxyphenol} \\ C. OH_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O H H CI H_{2} \\ \end{bmatrix} C. OH_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O CH_{2} \\ \end{bmatrix} C. OH \text{ or Oxyphenol} \\ C. OH_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O H H CI H_{2} \\ \end{bmatrix} C. OH_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O CH_{2} \\ \end{bmatrix} C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O CH_{2} \\ \end{bmatrix} C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix} O C. OH OX \text{ or } C_{6}H_$$

m-Amidophenol, melting at 122°, is obtained from m-nitrophenol (B. 11, 2101),

from the oxamic acid derivative of m-phenylenediamine (B. 28, R. 30), and by hearing resorcinol to 200° with ammonium chloride and aqueous ammonia. In this way the alkylamines yield the alkyl-m-amido phenols. The latter can also be obtained from the dialkyl-aniline-m-sulphonic acids (B. 22, 622).

Monoalkyl m amidophenols (B. 27, R. 953).—Dimethyl m amidophenol melts at 87°; diethyl-m amidophenol boils at 280°. m-Amidophenol and its alkyl derivatives are employed in the preparation of rhodamine dyes.

Consult B. 29, 501, for the action of phosgene upon the alkyl m-amidophenols.

Trimethyl-m-amidophenol, C₆H₄[1]OH[3]N(CH₂)OH—see B. 29, 1533.

p-Amidophenol melts at 184° with decomposition and sublimes. It results (1) from p-nitrophenol; (2) from 3 phenylhydroxylamine (p. 70); (3) by the action of the electric current upon nitrobenzene in strong sulphuric acid solution; its formation here is due to the rearrangement of the β -phenylhydroxylamine produced at first; (4) from [5] amidosalicylic acid. It is oxidized to quinone by chromic acid, or by PbO, and sulphuric acid. Bleaching lime converts it, as well as its substitution products, into quinone chlorimides. p-Amidophenol acts the same and just as readily as phenylhydrazine upon aldehydes

and ketones in dilute acetic acid (B. 27, 3005).

p-Amidophenetol, p-Phenetidine, NH₂[4]C₂H₄[1]OC₂H₅, is the ethyl ether. It boils at 242°. Boiling glacial acetic acid converts it into p-Acetamidophenetol, C₆H₄ NH. CO. CH₃, phenacetin, melting at 135°, which has been applied as an antiportal of the property of the pr tipyretic. Also p-Ethoxyphenylsuccinimide, Pyrantin, (CH₂CO)₂NC₂H₄OC₂H₅, meling at 155°, which, it is claimed, does not have the unpleasant action or after effects peculiar to phenacetin (B. 29, 84). p-Phenetolcarbamide, NH₂CO. NH[4]C₂H₄[1]OC₁II₅ (B. 28, R. 78, 83), has a very sweet taste. See p. 158 for Diamido-diphenyloxide-misland-market-labels (3). amidophenylsulphides.

m Oxydiphenylamine, C₆H₅NH[3]C₆H₄[1]OH, melting at 82° and boiling at 340°, and p Oxydiphenylamine, melting at 70° and boiling at 330°, are formed on heating resorcinol (p. 160) and hydroquinone with aniline and zinc chloride (B. 22, 2909). The oxydiphenylamines are intimately related to the indophenol-dyes. (See Quinones.)

Diamidophenois.—[2,4]-Diamidophenol, (NH₂),[2,4]C₈H₂[1]OH, is obtained from [2,4]-dinitrophenol, and by the electrolytic reduction of m-dinitrobenzene or m-nitroaniline in sulphuric acid (B. 26, 1848). The free base is very unstable, and its salts have been used as developers in photography under the name amidol. m-Anilido-p-phenitidine, $C_6H_5NH[3]C_6H_3$ { $\begin{bmatrix} 1\\ 4\end{bmatrix}NH_3$; see p. 155, under Hydrazine Phenols, for

its formation. Picramic Acid, [2]-Amido [3,4]-dinitrophenol, C₂H₂(NH₂). (NO₂)₂. OH, is obtained by evaporating ammonium picrate in alcoholic solution with ammonium sulphide. It

forms red needles, which melt at 165°.

[2,4,6] Triamidophenol, C₆H₂(NH₂)₃. OH, is obtained from picric acid by the action of phosphorus iodide, or by tin and hydrochloric acid (B. 16, 2400). When set free from its salts, it decomposes very quickly. Its salts, with three equivalents of acids, crystallize well. The HI-salt, C₆H₅O(NH₂)₃, 3HI, crystallizes in colorless needles. These salts color water which is faintly alkaline, and even spring water, a beautiful blue. If ferric chloride be added to the solution of the hydrochloride, it will become deep blue in color, and brown blue needles with metallic lustre will separate; they are HCl-amido di-imido-phenol, or diamidoquinone-imide (see this), which dissolves in water with a beautiful blue color.

An isomeric triamidophenol has been prepared by reducing diquinoyltrioxime (B. 30, 183).

[3,3,4,5]. Tetramidoanisol, (NH₂)₄C₆HOCH₃ (B. 25, 282).

Diazophenols.—Phenoldiazochlorides, HO. C₆H₄N₂Cl, result from the action of nitrous acid upon the hydrochlorides of the amidophenols. The free diazohydrates of the o- and namidophenols are resulted to the country of the the o and p-amidophenols seem to become anhydrides, in that the second affinity of the diazo-groups joins itself to the phenol hydrogen (B. 29, 1522):

$$C_{e}H_{4}\left\{ \begin{smallmatrix} N_{2}\\ O \end{smallmatrix} \right\}, \qquad C_{e}H_{2}Cl_{2}\left\{ \begin{smallmatrix} N_{2}\\ O \end{smallmatrix} \right\}, \qquad C_{e}H_{3}(NO_{2})\left\{ \begin{smallmatrix} N_{2}\\ O \end{smallmatrix} \right\}.$$

p-Diazophenol Cyanide, HO[4]C₆H₄N₂. CN, from the action of potassium cyanide on the chloride, consists of yellow needles. Caustic potash saponities it to the potassium salt of diazophenolearboxylic acid, HO. C₆H₄N₂COOH. Dibromphenoldiazo-sulphonic Acid, C₆H₂Br₂(OH)N₃SO₃H + 2H₂O, can be isolated from its potassium salt produced from the interaction of potassium sulphite and dibromphenoldiazochloride.

p-Phenoldiazomercaptan Hydrosulphide, CaH4(OH). N2SH.SH2, from the action of hydrogen sulphide upon diazophenol solutions, consists of red needles melting at 75°

with decomposition (B. 28, 3250).

Hydrazine Phenols.—The free bodies are exceedingly unstable.

o-Hydrasine Anisol, NH₂NH[2]C₆H₄[1]OCH₃, melts at 43° and boils at 240° (A. 221, 314). Benzene-p-hydrazine phenol ethers result from the reduction of the alkyl ethers of the oxyazobenzenes or azophenols; they show the semidine rearrangement when acted upon with stannous chloride and hydrochloric acid (p. 117). Thus, benzene p-hydrazophenetol changes to m-ethoxy-o-amidodiphenylamine (B. 27, 2700; 28, R. 753; 29,

$$C_{\mathbf{6}}H_{\mathbf{5}}NHNH[1]C_{\mathbf{6}}H_{\mathbf{4}}[4]OC_{\mathbf{2}}H_{\mathbf{5}} \xrightarrow{\qquad \qquad } C_{\mathbf{6}}H_{\mathbf{5}}^{NH}[1] \\ NH_{\mathbf{1}}[2] \Big\} C_{\mathbf{6}}H_{\mathbf{5}}[5]OC_{\mathbf{1}}H_{\mathbf{5}}.$$

Azophenols, Oxyazobenzenes.—Formation. (1) From diazo-salts and monohydric phenols, m-dioxybenzenes, m-amidophenols, and m-phenolsulphonic acids:

$$C_8H_6N = N \cdot NO_8 + C_6H_6OH = C_6H_5N = N[1]C_6H_6[4]OH.$$

The solution of the diazo-salt is allowed to run into the alkaline phenol solution while cooling and stirring. Phenoldisazobenzene is produced together with phenolazobenzene.

As with the amidoazo-compounds, the entering diazo-group arranges itself in the phenols in the p-position, and when this is already occupied it takes the o-position with reference to the hydroxyl group (B. 17, 876; 21, R. 814).

(2) By heating the diazoamidobenzenes with monohydric phenols, and also with resorcinol (B. 20, 372, 904, 1577):

$$C_6H_6N_2$$
. NH. $C_6H_5 + C_6H_5$. OH = C_6H_5 . N_2 . C_6H_4 OH + C_6H_5 . NH₂.

(3) By the molecular rearrangement induced by heating azoxybenzenes with sulphuric acid (B. 14, 2617):

$$C_6H_6$$
. N
 C_6H_6 . N
 C_6H_6 . N_2 . C_6H_4 OH

Azoxybenzene

Oxyazobenzene.

(4) By reduction of the nitrophenols in alcoholic potassium hydroxide solution.

(5) By the action of anilines upon nitrosophenols.

Constitution.—The oxyazo-compounds, containing hydroxyl in the ortho-position to the azo-group, are probably quinone-hydrazones:

$$C_{6}H_{4}^{\left\{ [1]OH \atop \left[2\right]N=N \right.}C_{6}H_{4}^{\left\{ [1]:O \atop \left[2\right]:N-NHC_{6}H_{5} \right.} \text{ or } C_{6}H_{4}^{\left\{ [1]O \atop \left[2\right]:N-NH.C_{6}H_{5} \right.}$$
o-Oxyazobenzene Quinonephenyl-hydrazone.

This seems to be evident both from their cryoscopic and chemical behavior (B. 28,

2415; 29, 2361); compare also naphthoquinonehydrazones.

p-Oxyasobenzene, Benzene-p-azophenol, $C_6H_5N=N[1]C_6H_4[4]OH$, melting at 148°, crystallizes in orange-yellow needles. It is produced by the methods mentioned in connection with oxyazo-derivatives; treated with phosphorus pentachloride, and then with water, it is converted into the phosphoric ester, PO(OC₆H₄N₂C₆H₅)₃, melting at 148° (B. 24, 365). Benzene-p-azophenetol melts at 77° (B. 25, 994). p-Azophenol, HO[4]C₆H₄[1]N₂[1]C₆H₄[4]OH, melting at 204°, consists of light-brown crystals. It is produced:

(I) By fusing p-nitro- and nitroso-phenol with caustic alkali.

(2) By the pairing of diazobenzene nitrate with phenol.

(3) From p-oxyazobenzene-sulphonic acid (B. 15, 3037). See B. 17, 351, for the azo- and diazo-derivatives of the cresols.

The sulpho-acids of the oxyazohenzenes are dyes—e.g., p-Sulpho-benzene-p-azo-phenol, $SO_3H[4]C_6H_4[1]N=N[2]C_6H_4[4]OH$, from p-oxyazobenzene and sulphuix acid, and from p-diazohenzene-sulphonic acid by means of sodium phenate, is tropechiae Y (from yellow) of commerce (B. 11, 2192). Also compare resorcinol.

Sulphonic Acids of Phenol.—The sulphonation of phenol proceeds with the replacement of the o- and p-hydrogen atoms, just as in the nitration process (the sulpho-groups enter the meta-position with reference to one another):

$$C_{\mathbf{6}} H_{5} \mathrm{OH} \left\{ \begin{matrix} \longrightarrow C_{\mathbf{6}} H_{4} \left\{ \begin{bmatrix} \mathbf{1} \end{bmatrix} \mathrm{OH} \\ \mathbf{2} \end{bmatrix} \mathrm{SO}_{\mathbf{1}} H - \mathbf{1} \\ \longrightarrow C_{\mathbf{6}} H_{4} \left\{ \begin{bmatrix} \mathbf{1} \end{bmatrix} \mathrm{OH} \\ \mathbf{4} \end{bmatrix} \mathrm{SO}_{\mathbf{3}} H - \mathbf{1} \end{matrix} \right\} \longrightarrow C_{\mathbf{6}} H_{\mathbf{3}} \left\{ \begin{matrix} \mathbf{1} \end{bmatrix} \mathrm{OH} \\ \mathbf{2} \end{bmatrix} \mathrm{SO}_{\mathbf{3}} H - \mathbf{1} \\ \mathbf{4} \end{bmatrix} \mathrm{SO}_{\mathbf{3}} H - \mathbf{1} \\ \mathbf{4} \end{bmatrix} \mathbf{C}_{\mathbf{6}} H_{\mathbf{3}} \left\{ \begin{matrix} \mathbf{1} \end{bmatrix} \mathrm{OH} \\ \mathbf{4} \end{bmatrix} \mathrm{SO}_{\mathbf{3}} H - \mathbf{1} \\ \mathbf{4} \end{bmatrix} \mathbf{C}_{\mathbf{6}} H_{\mathbf{3}} \left\{ \begin{matrix} \mathbf{1} \end{bmatrix} \mathrm{OH} \\ \mathbf{4} \end{bmatrix} \mathbf{C}_{\mathbf{6}} H_{\mathbf{3}} \left\{ \begin{matrix} \mathbf{1} \end{bmatrix} \mathrm{OH} \\ \mathbf{4} \end{bmatrix} \mathbf{C}_{\mathbf{6}} H_{\mathbf{3}} \left\{ \begin{matrix} \mathbf{1} \end{bmatrix} \mathrm{OH} \\ \mathbf{4} \end{bmatrix} \mathbf{C}_{\mathbf{6}} H_{\mathbf{3}} \left\{ \begin{matrix} \mathbf{1} \end{bmatrix} \mathrm{OH} \\ \mathbf{4} \end{bmatrix} \mathbf{C}_{\mathbf{6}} H_{\mathbf{3}} \left\{ \begin{matrix} \mathbf{1} \end{bmatrix} \mathrm{OH} \\ \mathbf{1} \end{bmatrix} \mathbf{C}_{\mathbf{6}} H_{\mathbf{3}} \left\{ \begin{matrix} \mathbf{1} \end{bmatrix} \mathrm{OH} \\ \mathbf{1} \end{bmatrix} \mathbf{C}_{\mathbf{6}} H_{\mathbf{3}} \left\{ \begin{matrix} \mathbf{1} \end{matrix} \mathbf{C}_{\mathbf{6}} H_{\mathbf$$

o- and p-Phenolsulphonic Acids are formed when phenol dissolves in concentrated sulphuric acid; at medium temperatures the former is the more abundant, but readily passes into the para- on the application of heat, or even upon boiling with water. o-Phenetolsulphonic acid is just as easily changed to the p-acid by heating it to 100° (B. 27, R. 591).

The acids are separated through their potassium salts. On allowing to crystallize the potassium salt of the para-acid first separates in hexagonal plates; later the ortho-salt, C6H4(OH). SO2K + 2H2O, crystallizes out in prisms, which soon efforesce on exposure (A. 205, 64).

The free acids can be obtained in crystalline form by the slow evaporation of their aqueous solution. The aqueous solution of the ortho-acid is applied as an antiseptic under the name of aseptol (B. 18, R. 506). The para acid yields quinone if its sodium salts be oxidized with MnO, and sulphuric acid. When the ortho-acid is fused with KOII at 310° it yields pyrocatechin—o-dioxybenzene; the para-acid does not react at

320°, and at higher temperatures yields diphenols. (See Diphenyl.)

The iodation of the para-acid produces [2,6]-Di-iod-phenolsulphonic Acid, C₆H₂.

[3, (OII). SO₃H. This is applied as an antiseptic, bearing the name sozo-iodol (B. 21,

Ř. 250).

Meta-phenolsulphonic Acid [1,3] is produced when meta-benzene-disulphonic acid (p. 135) is heated to 170–180° with aqueous potassium hydroxide (B. 9,969). The free acid contains two molecules of H₂(). Fusion with potassium hydroxide at 250° converts it into resorcinol [1,3]. When para-benzene-disulphonic acid is heated with caustic alkali, meta-phenol-sulphonic acid is also produced at first, but it yields resorcinol later.

Phenol [2,4] disulphonic Acid results from the action of an excess of sulphunc acid upon phenol, also upon [1,2]- and [1,4] phenol-sulphonic acid. The solutions of the acid and its salts are colored a dark red by ferric chloride.

Phenol [2,4,6] trisulphonic Acid is obtained when concentrated sulphuric acid and P2O3 act upon phenol. It crystallizes in thick prisms with 31/2H2O.

See B. 28, R. 378, 399, for the amidophenol-sulphonic acids.

THIO-DERIVATIVES OF PHENOL.

Mercaptans.—Thiophenol, *Phenylmercaptan* [*Phenthiol*], C₈H₈SH, boiling at 168°, with sp. gravity 1.078 (14°), is a mobile, ill-smelling liquid. It is made (1) by letting P₂S₅ act upon phenol (Z. f. Ch. 1867, 193); (2) by distilling sodium benzene sulphonate with potassium sulphydrate (B. 17, 2080); (3) from phenyldithiocarbonic

ters (see below). It manifests great tendency to throw off hydrogen and become henyldisulphide; hence it often acts as a reducing agent (compare B. 29, R. 979). **Mercury Thiophenate, (CaH5S), Hg. Thiophenyl Acetal, CaH5. S. CH2. CH(OC2H5), oils at 273° (B. 24, 160). Thiophenylacetone melts at 34° and boils at 266° (B. 24, 63). Consult B. 24, 234; 28, 1120; A. 253, 161, for mercaptal (1, 204) and mercapol derivatives of thiophenol. **Phenyl Orthothioformic Ester, CaH5. CO2. C2H5, boils a 260° (B. 19, 1228). **Phenyldithiocarbonic Ester, CaH6S. CSOR, is formed from liazobenzene chloride and represents a common reaction. It yields thiophenol when apponified. This is the most convenient way of preparing thiophenols (B. 21, R. 915). **Diazobenzene Thiophenyl Ester, C.H.N., SC.H., an oil, is produced from diazobenzene Diazobenzene Thiophenyl Ester, CeH5N2. SC2H5, an oil, is produced from diazobenzene chloride and phenylmercaptan (B. 28, 3237).

o-Thiocresol melts at 15° and boils at 188°; the m-body is a liquid boiling at 195-205°.

while the p-compound melts at 43° and boils at 194°. Thiocymene, (CH3)(C3H7)C8H2SH

(see carvacrol, p. 145).

Mention should be made of o-amidothiophenol, one of the numerous substitution

products of thiophenol, because of its heterocyclic condensation products.

o-Amido-thiophenol, NH₂[2]C₄H₄[1]SH, is obtained from ortho-nitro-benzenesulphonic chloride by reduction with tin and hydrochloric acid. A better method to pursue is to fuse benzenyl-o-amidothiophenol with caustic potash (B. 20, 2259). It melts at 26° and boils at 234°

m-Amidothiophenol (B. 27, 2816).

The condensations of the o-Amidothiophenols (compare o-diamines, p. 95 and c-amidophenols (p. 153). (1) Benzothiazoles are formed on heating o-amidothiophenol with carboxylic acids, acid chlorides, or acid anhydrides. (2) o-Amidothiophenol, by the action of chlorcarbonic esters, forms μ-οχυβενισοτhiazole or carbonylamidothiophenol. (3) Carbon disulphide produces μ-sulphydrobenzothiazole (see this). (4) Nitrous acid converts o-amidothiophenol into o-phenylene diazosulphide (see this); at 200-220° this becomes diphenylene disulphide :

$$C_{6}H_{4}\left\{ \begin{bmatrix} 1 \end{bmatrix}SH \\ CS_{2} \\ NOOH \\ C_{6}H_{4} \\ CS_{2} \\ NOOH \\ C_{6}H_{4} \\ CS_{2} \\ CS_{6}H_{4} \\ CS_{6$$

Phenylsulphocarbazine (p. 127) is also a heterocyclic derivative of o-amidothiophenol. See p. 160 for the condensation of o-amidothiophenol with pyrocatechol to thiodiphenylamine.

Sulphides.—Phenyl Disulphide, (C₆H₈)₂S₂, melting at 61° and boiling at 310°, results from the oxidation of thiophenol with a chromic acid mixture or in ammoniacal solution by the oxygen of the air; by the action of iodine upon aqueous potassium thio-phenate; by heating thiophenol with benzene sulphinic acid; by heating thiophenol or phenylsulphide with sulphur, etc. Reducing agents decompose it into two molecules of thiophenol, and alcoholic potash breaks it down into potassium thiophenate and potassium benzene sulphinate.

Phenyl Sulphide, (C_aH₅),S, Benzene sulphide, a colorless liquid with an odor resembling that of leeks, boils at 292° and has a specific gravity of 1.12. It is formed (1) by distilling phenol with P₂S₅ (along with thiophenol); (2) in the distillation of sodium benzene sulphonate, as well as in the action of benzene diazochloride upon sodium thiophenate with P.S. (B. 23, 2471); (3) on heating sulphur with diphenyl-

54:

sulphone (method of preparation), into which it is also converted by oxidants (B. 26.16); (4) upon heating mercury diphenyl with sulphur (B. 27, 1771); (5) phenyl sulphide and its homologues are also readily prepared by heating aromatic lead mercaptides with haloid benzenes (the bromides are the best adapted for this purpose) (B. 26.12). Diphenylene sulphide or diben-othiophene (see this) is produced on conducting

the vapors of phenylsulphide through a tube heated to redness.

Amidophenyl Sulphides or Thioanilines.—Formation: (1) These compounds result when nitrothiophenyls are reduced (comp. B. 29, 2362); (2) from anilines by boiling the latter with sulphur and lead oxide (B. 4, 384). Sulphur chloride converts the dialkylanilines into sym.-p-tetra-alkyl-diamidophenyl sulphides. Silver nitrate and ammonia desulphurize the tetra-alkyl compounds, with the formation of sym.-p-tetra-alkyl-diamidodiphenylene oxides—e. g., O[C₆H₆[4]. N(CH₃)₂]₂ (B. 21, 2056). Upon heating methyl-thio-anilines—e. g., thio-p-toluidine—with sulphur whigher temperatures, thiazole derivatives, like dehydrothiotoluidine (see benzothiazole), are produced.

p-Diamidodiphenyl Sulphide, S<C₈H₄. NH₂, Thioaniline, melts at 105°. o-Diamidodiphenyl Sulphide melts at 93° (B. 27, 2807). See B. 29, 2774 for isomeric thioanilines, melting at 80° and 86°.

Thio-p-toluidine, $S < {C_8H_3(CH_3) \cdot NH_4 \cdot NH_4}$. Diamidoditolyl Sulphide, melts at teg⁴. The sodium salts of thio- and dithio-toluidine sulphonic acids dye unmordanted cotton (B. 21, R. 877). They are, therefore, so-called substantive cotton dyes.

The bis-diazo salts of thio-p-toluidine combine with naphthylamine-sulphonic acids

and yield diazo dyes of a brown-red color (B. 20, 664).

Thiodiphenylimides.—Thiodiphenylamine, $S\left\{\begin{bmatrix}1\\I\\C_0H,\begin{bmatrix}2\\I\end{bmatrix}\right\}$ NH, is the simplest of these heterocyclic bodies. Methylene blue, a most valuable dye, is derived from it. The thiophenylamine group will be discussed later with the hetero six-ring compounds.

Thioanisol, S(C₆H₄OCH₃)₂, melting at 46°, and allied bodies are formed when thionyl chloride or sulphur chloride with aluminium chloride acts upon the phenol-ethers (A. 27.

2540).

Phenylselenides and tellurides are quite readily obtained from the mercury diphenyl

compounds by the action of selenium and tellurium.

Diphenviselenide, $(C_6H_5)_3$ Se, also results upon heating selenium with diphenylsulphone. Sulphur dioxide escapes at the same time. It boils at 163° (14 mm.). Further action of selenium produces diphenyldiselenide, $(C_6H_5)_3$ Se, melting at 63° and boiling at 203° (11 mm.). Reduction changes it to two molecules of phenylselenium hydrum. C_6H_5 SeH, melting at 183°. Diphenyltelluride, $(C_6H_5)_3$ Te, boils at 174° (10 mm.) B. 28, 1670; 29, 428.

DIHYDRIC PHENOLS.

Several representatives of this family occur in plants, or have obtained as decomposition products of plant substances. Reserve m-dioxybenzene is especially important from a technical standard

The general methods of formation are like those of the corresponding phenois—(1) by fusing monohalogen phenois, laterated phenois acids, phenoisulphonic acids and honorard with potassium hydroxide (pp. 135) amido-phenois; and (3) by the dry alone or with lime or baryts.

(4) o- and p-Dioxybenze their corresponding quir

Deportment. - The

of the two hydroxyl groups with reference to one another. The three

implest dioxybenzenes:

Pyrocatechol [1,2], Resorcinol [1,3], Hydroquinone [1,4], are, therefore, ypical representatives of the three groups of dihydric phenols. portment of such bodies can be fully illustrated through them. lihydric phenols can be changed by chlorine to hydroaromatic ketochlorides, whose carbon ring may be readily ruptured (see p. 44). Chloroform and caustic potash convert them into dioxyaldehydes, while they yield dioxycarboxylic acids with carbon tetrachloride and caustic potash.

Pyrocatechin Group.—All o-dioxybenzenes are colored green by ferric chloride. They are further distinguished from the m- and p-compounds by their ability to readily exchange their hydroxyl hydrogen atoms and

thus form cyclic esters.

Pyrocatechin, Pyrocatechol. o-Dioxybenzene, [1,2-Phendiol] C₆H₄[1,2](OH)₂, melting at 104° and boiling at 245°, was first (Reinsch, 1839) obtained in the distillation of catechine (the juice of Mimosa catechu), and also from Moringa tannic acid.

It is produced in fusing many resins with caustic potash. It occurs in kino, the dried juice of different kinds of Pterocarpus, Butea, and Eucalyptus, in beechwood tar, and has been obtained as a by-product in the manufacture of paraffin from bituminous shales ut the Messel mine, near Darmstadt, etc. Pyrocatechol-sulphuric Acid occurs in the arine of the horse and in that of man. It is artificially made (1) by oxidizing phenol with hydrogen peroxide; (2) by the distillation of protocatechuic acid, or [ICO2H, 3,4]dioxybenzoic acid; (3) by fusing [1,2]-chlorphenol, [1,2]-bromphenol (B. 27, R. 957, D. P. 76,597), [1,2]-benzene disulphonic acid, and [1,2]-phenolsulphonic acid with caustic potash; (4) by heating guaiacol pyrocatechol monomethyl ether (see this) to 2000 with hydriodic acid.

On exposure to the air its alkaline solutions assume a green, then brown, and inally a black color. Lead acetate throws out a white precipitate, PbC₈H₄O₂, from its squeous solution. Neither resorcinol nor hydroquinone shows this reaction. Pyrocaechin reduces cold silver solutions and alkaline copper solutions. The application of heat is required in the latter case. Pyrocatechin in glacial acetic acid solution is conrested by chlorine into tetrachlorpyrocatechin, tetrachlor-o-quinone (p. 169), and hexahlor-o-diketo-R-hexene (p. 45). In nitrous acid to dioxytartaric acid. Consult p. 160
or the heterocyclic formations obtainable from pyrocatechol. Heated with phthalic
unhydride and sulphuric acid, it yields alisarine (see this) and hystasarine (see this).
Compare protocatechuic aldehyde and protocatechuic acid.

Ethers.—The monomethyl ether, HO[1]C₆H₄[2]OCH₃, melting at 28° and boiling at 250°, Guaiacol, occurs in the creosote from beechwood tar (B. 28, R. 156). It is produced on heating pyrocatechin with potassium hydroxide and potassium methyl sul-hate to 180°, as well as by heating calcium vanillate, and from veratrol (B. 28, R. 362). ferric chloride gives its alcoholic solution an emerald-green color (see vanillin).

Dimethyl ether, Veratrol, C₆H₄[1,2](OCH₃)₂, melting at 15° and boiling at 205°, is wepared by treating the potassium salt of the monomethyl ether with CH₃I, and by listilling vetraric acid with lime. The ethylene ester boils at 216° (A. 280, 205).

Pyrocatechin sulphite boils at 210-211° (B. 27, 2752); pyrocatechin chlorphosphine nelts at 130°; pyrocatechin oxychlorphosphin melts at 35° (B. 27, 2569) (see below).

Diacetyl ester, C₆H₄[1,2](OCCH₃)₂.

The carbonic ester, C_6H_4 $\left\{\begin{bmatrix} 1 & 0 \\ 2 & 0 \end{bmatrix}$ CO, results from the action of chlorcarbonic ester pon pyrocatechin, melts at 118° and boils at 227° (B. 13, 697; A. 226, 84). Monobenzoyl ster melts at 130° (B. 26, 1076). Dibensoyl ester melts at 84° (A. 210, 261). Hetero-ring Formations from Pyrocatechol.—By the replacement of both hydroxyl hydrogen atoms of pyrocatechol cyclic esters are formed with SOCl₂, PCl₃, POCl₃, COCl₂, and ethylene bromide. o-Phenylenediamine, o-amidophenol, and o-amidothiophenol condense with pyrocatechin, forming phenazine, phenoxasine, and thiodiphenylamine:

$$C_{6}H_{4}\left\{ \begin{bmatrix} 1\\2\\2\\0 \end{bmatrix}O > SO \qquad \qquad \begin{array}{c} \text{Pyrocatechol Sulphite} \\ \text{Pyrocatechol Chlorphosphine} \\ \text{PoCl}_{8} \longrightarrow C_{6}H_{4}\left\{ \begin{bmatrix} 1\\2\\2\\0 \end{bmatrix}O > PCl \qquad \qquad \begin{array}{c} \text{Pyrocatechol Chlorphosphine} \\ \text{Pyrocatechol Oxy-chlorphosphine} \\ \text{Pyrocatechol Carbonate} \\ \text{Pyrocatechol Carbonate} \\ \text{Pyrocatechol Carbonate} \\ \text{Pyrocatechol Ethylene Ether} \\ \text{C}_{6}H_{4}\left\{ \begin{bmatrix} 1\\2\\2\\0 \end{bmatrix}O = CC \\ \text{Pyrocatechol Carbonate} \\ \text{Pyrocatechol Ethylene Ether} \\ \text{C}_{6}H_{4}\left\{ \begin{bmatrix} 1\\2\\2\\0 \end{bmatrix}O = CC \\ \text{Pyrocatechol Ethylene Ether} \\ \text{C}_{6}H_{4}\left\{ \begin{bmatrix} 1\\2\\2\\0 \end{bmatrix}O = CC \\ \text{Pyrocatechol Ethylene Ether} \\ \text{Pyrocatechol Ethylene Ether} \\ \text{C}_{6}H_{4}\left\{ \begin{bmatrix} 1\\2\\2\\0 \end{bmatrix}O = CC \\ \text{Pyrocatechol Ethylene Ether} \\ \text{Phenazine} \\ \text{NH}_{4}\left\{ \begin{bmatrix} 1\\2\\0 \end{bmatrix}O = CC \\ \text{Pyrocatechol Ethylene Ether} \\ \text{Phenazine} \\ \text{NH}_{4}\left\{ \begin{bmatrix} 1\\2\\0 \end{bmatrix}O = CC \\ \text{Pyrocatechol Ethylene Ether} \\ \text{Phenazine} \\ \text{NH}_{4}\left\{ \begin{bmatrix} 1\\2\\0 \end{bmatrix}O = CC \\ \text{Pyrocatechol Carbonate} \\ \text{Pyrocatechol Carbonate} \\ \text{Pyrocatechol Ethylene Ether} \\ \text{Phenazine} \\ \text{NH}_{4}\left\{ \begin{bmatrix} 1\\2\\0 \end{bmatrix}O = CC \\ \text{Pyrocatechol Carbonate} \\ \text{Pyrocatechol Ethylene Ether} \\ \text{Phenazine} \\ \text{NH}_{4}\left\{ \begin{bmatrix} 1\\2\\0 \end{bmatrix}O = CC \\ \text{Pyrocatechol Carbonate} \\$$

Homologous Pyrocatechols.—Isohomopyrocatechol, CH₃[1]C₆H₃[2,3](OH)₂, melts at 47° (B. 24, 4137). Homopyrocatechol, CH₃[1]C₆H₃[3,4](OH)₂, melting at 51° and boiling at 251°, occurs in the form of its 3-methyl ether as creosol, CH₃[1]C₆H₃[3]-(OCH₃)[4]OII, boiling at 221°, in beechwood tar, together with phloral (B. 14, 2005).

Creosol is also formed together with guaiacol (see above) in the distillation of guaiacol resin. Higher homologues of pyrocatechol have been obtained by treating pyrocatechol with alighbrid alcohols and zinc chloride (B. 28, R. 312; D. P. 78, 882).

with aliphatic alcohols and zinc chloride (B. 28, R. 312; D. P. 78,882).

Monothiopyrocatechol, C₆H₄[1,2](SH)(OH), melting at +5° and boiling at 217°, results from the reduction of diphenoldisulphide, [C₆H₄OH]₂S₂, produced on heating sodium phenoxide with sulphur.

Diphenylene Disulphide, or Thianthrene, $C_6H_4\left\{\begin{bmatrix}\mathbf{I} & \mathbf{S} & \mathbf{I} \\ \mathbf{2} & \mathbf{S} & \mathbf{I}\end{bmatrix}\right\}C_6H_4$, melting at 158° and boiling at 360°, should be regarded as a derivative of dithiopyrocatechol, $C_8H_4(SH)_r$. It is made by boiling phenylsulphide with sulphur, also from benzene, SCl_9 , and aluminium chloride, as well as by heating phenylene diazosulphide (p. 157). Oxidation converts it into a disulphone, $C_6H_4(SO_2)_2C_9H_4$. When the latter is heated with selenium Diphenylene Disclenide, selenanthrene, $C_6H_4:(Se_2):C_6H_4$, melting at 181° and boiling at 223°(11 mm.), results (B. 29, 435, 443).

Resorcinol Group.—Resorcinol and many of its homologues combine with phthalic anhydride, the products being the *fluoresceins* (see these). The aqueous solutions of the m-dioxybenzenes are colored *dark violet* by ferric chloride.

Resorcinol, C₆H₄[1,3](OH)₂, melting at 118° and boiling at 276°, is produced from Galbanum, Asafwtida, and other resins upon heating them with potash, as well as by distilling the extract of Brazil-wood. It can also be obtained from many m-disubstitution-products of benzene, such as [1,3]-chlor- and iodphenol, [1,3]-phenolsulphonic acid, [1,3]-benzene-disulphonic acid, etc., on fusing them with potash or soda at 230-280°; by the same method from umbelliferone.

Even o- and p-compounds (B. 7, 1175; 8, 365), especially when fused at high temperatures with caustic alkali, yield resorcinol; hence the potash fusion is not available in the determination of position (p. 149). Resor-

cinol is made on a technical scale from m-benzene-disulphonic acid

(J. pr. Ch. [2] 20, 319).

Properties and Deportment.—Resorcinol crystallizes in rhombic prisms It dissolves readily in water, alcohol, and ether, but not in chloroform and carbon disulphide. It possesses a sweet taste. Lead acetate does not precipitate its aqueous solution (distinction from pyrocatechin).

Sodium amalgam reduces resorcinol to dihydroresorcin (A. 278, 20), or m-diketohexamethylene (B. 27, 2129). Bromine precipitates it from aqueous solution as tribrom-resorcinol, melting at 111°, while chlorine converts it in glacial acetic acid solution finally into heptachlor-resorcinol (p. 46) (B. 26, 498), which can be easily decomposed. Fusion with caustic soda produces phloroglucin, pyrocatechol, and diresorcinol, (HO)₂C₄H₃ — C₄H₅(OH)₂ (B. 26, R. 233). The chlorhydrate of a triresorcinol, C18H14O4 (A. 289, 61), is formed when resorcinol is heated with hydrochloric acid.

Fluorescein is produced when resorcinol is heated with phthalic anhydride. If resorcinol be heated with sodium nitrite, it forms a deep-blue dye, soluble in water. Acids turn this red (B. 17, 2617). It is used as an indicator under the name of lacmoid (B. 18, R. 126). Nitric acid, containing nitrous acid, converts resorcin into two dyes,-

resormin and resormin,—derivatives of phenoxazine (see this) (B. 23, 718).

When diazo-salts act upon aqueous or alkaline resorcinol solutions, azodyes and

disazodyes are produced; thus, with diazobenzene nitrate or chloride the products are:

Benzeneasoresorcinol, (C₆H₅N₂)C₆H₃(OH)₂, a- and β-diazobenzene-disazoresorcinol, (C₆H₅N₂)₂C₆H₂(OH)₂ (B. 15, 2816; 16, 2858; 17, 880); while with the diazochloride of amidoazobenzene there results azobenzene-azo-resorcinol, C₆H₅N₂. C₆H₄N₂. C₆H₃(OH)₂ (B. 15, 2817).

Ethers and Esters.—The monomethyl ether boils at 243° (B. 16, 151). The dimethyl ether boils at 214° (B. 10, 868). The diacetyl ester boils at 278° (B. 16, 552). The dicarbonic ester, C₆H₄(OCO₂C₂H₅), boils at 300° (B. 13, 697). The dibensoate melts at 117° (A. 210, 256). Resorcinol combines with the various sugars under the influence of hydrochloric acid (B. 27, 1356).

Dinitroso-resorcinol, diquinoyldioxime, C₆H₂[1,3](OH)₂[4,6](NO)₂ or C₆H₂(O)₃ (N.OH),[1,3,2,4], crystallizes in yellow brown leaflets, which detonate on heating to 115° C. (B. 20, 3133). It occurs in commerce under the names solid green, or chlorine.

Nitric acid vapors oxidize resorcinol to v-dinitroresorcin, (NO₂)₂[2,4]C₆H₂[1,3](CH)₃, melting at 115°. Isodinitroresorcin, Styphnic Acid, Oxypicric Acid, (NO₂)₂-[4,6]C₆H₂[1,3](OH)₃, melts at 212°.

When cold nitric acid acts on resorcinol and various gum-resins (galbanum, etc.), or by nitrating metanitrophenol and various dinitrophenols, we get Trinitroresorcinol, (NO₃)₈[2,4,6]C₈H[1,3](OH)₉. It melts at 175°. Ferrous sulphate and lime-water color it green (picric acid colors it blood red). The diethyl ester melts at 120°.

Thioresorcinol, C₆H₄[1,3](SH)₄, melts at 27°, and boils at 243°. It results from the reduction of benzene-m-disulphonic chloride, and when heated with phenylisocyanate, becomes bisphenylearbamate, CaH4(SCONHCaH5)2, melting at 179° (B. 29, R. 177).

Homologous Resorcinols.—Orcinol is by far the most important body among those which follow:

	N	I.P. B.P.	
Orcipol,	CH ₃ [1]C ₆ H ₃ [3,5](OH) ₆	07° 289°	•
		269°	⁹ (B. 19, 136).
	. CH ₂ [1]C ₄ H ₃ [2,6](OH),	54° —	(B. 17, 1963).
2.4 Dioxy-m-xylene,	. (CH ₃),[1,3]C ₆ H ₂ [2,4](OH), 1	47° 149	B. 23, 3114).
m-Xylorcin.	(CH _s) ₂ [1.3]C ₆ H ₂ [4,6](OH), 1	25° 277	°) (B. 19,
β-Orcin	(CH.),[1.4]C,H.[3.5](QH). I	63° 279'	° (2318).
Mesorcin.	(CH ₃),[1,3,5]C,H(OH), 1	49° 275°	(A. 215, 100).
Ditertiary-amylresorc	(inol, $(C_8H_{11})_2C_6H_2[1,3](OH)_4$	89° —	(B. 25, 2653).
11-14	7.	•	•

Orcin, Orcinol, CH₃[1]C₂H₃[3,5](OH)₃, is the most important of the six theoretically possible and known dioxytoluenes (B. 15, 2995). It is found in many lichens of the variety Roccella and Lecanora, partly free and partly as orsellic acid, or partly as erythrine or diorsellic erythric ester. It is obtained from orsellic acid either by dry distillation or by boiling with lime.

It is obtained by fusing the extract of aloes with caustic potash. It can be prepared synthetically from 3,5 dinitro-p-toluidine and various other toluene-derivatives by the re-

placement of their side groups by hydroxyl groups (B. 15, 2990).

Orcin is produced in the distillation of o-dioxyphenylacetate of silver, (HO)₂[3,5]C₁: II₃[1]CH₂. CO₂Ag (B. 19, 1451), and upon heating dehydracetic acid (see vol. I) with concentrated caustic potash (B. 26, R. 316). Orcin crystallizes in colorless, six-sided prisms containing one molecule of water. It dissolves easily in water, alcohol, and ether, and has a sweet taste. It melts at 56°, when it contains water, but gradually loses this, and melts (dried in the desiccator) at 107°. It boils at 290°. Lead acetate precipitates its aqueous solution; ferric chloride colors it a blue violet. Bleaching lime causes a rapidly disappearing dark-violet coloration. It yields azo-coloring substances with diazo-compounds, and therefore has the 2OH-groups in the meta-position (p. 154). It does not form a fluorescein with phthalic anhydride (p. 160). Chlorine changes it, when dissolved in glacial acetic acid, into trichlororcin, melting at 127°. Dissolved in chloroform it is converted by the same reagent into pentachlororcin, or [1,3,5]-dikto-methylpentachlor-R-hexene (B. 26, 317) (p. 46).

methylpentachlor-R. Aexene (B. 26, 317) (p. 46).

Nitroso-orcin, CH₂. C₂H₂(OH)₂(NO), consists of two modifications—dark-red crystals and bright-yellow needles; the first change to the second when heated to 100-110°

(B. 29, 989).

On allowing its ammoniacal solution to stand exposed to the air, orcinol changes to orcein, $C_{20}H_{14}N_1O_7$ (B. 23, R. 647), which separates out in the form of a reddish-brown amorphous powder. It dissolves in alcohol and alkalies with a dark-red color, and is reprecipitated by acids. Orcein forms red lac-dyes with metallic oxides. It is the chief constituent of the coloring-matter archil (called also persio, cudbear, and purpur—French) which originates from the same lichens as orcinol through the action of ammonia and air. Litmus is produced from the lichens Roccella and Lecanora by the action of ammonia and potassium carbonate. The concentrated blue solution of the potassium salt, when mixed with chalk or gypsum, constitutes the commercial litmus.

Iso-orcin (Cresorcin, γ -orcin), is obtained by fusing 2,4-toluene disulphonic acid with KOII.

p-Xylorcin, or β -Orcin, from m-dinitro-p-xylene, rapidly acquires a red color on exposure to air containing ammonia. It has been obtained by distillation from various lichen acids—e. g., usnic acid. Mesorcin, or dioxymesitylene, is made from dinitro-mesitylene.

Hydroquinone Group.—The p-dioxybenzenes are usually called hydroquinones, because they are easily obtained by the reduction of the pquinones, and just as readily reconverted into the latter by ferric chloride.

Hydroquinone, p-Dioxybenzene, C,H,[1,4](OH), melting at 169°, was first obtained by the dry distillation of quinic acid and by digesting its aqueous solution with lead dioxide (Wöhler, A. 65, 349):

$$C_6H_7(OH)_4COOH + O = C_6H_4(OH)_2 + CO_2 + 3H_2O.$$

It results also, together with glucose, on boiling the glucoside arbutin with dilute sulphuric acid, and occurs in *Protea mellifera* (B. 29, R. 416).

It is further formed by the electrolytic oxidation of an alcoholic benzene solution acidulated with sulphuric acid (B. 27, 1942), and by fusing [1,4]-iodphenol with potassium hydroxide at 180°; or from [2,5]-oxysalicylic acid, and from para-amidophenol; also in small quantities in the distillation of succinates. The most convenient method of preparing it consists in reducing quinone with sulphurous acid:

Extract the hydroquinone from the aqueous solution by shaking with ether, and purify the product by recrystallization from hot water that has passed through animal charcoal

(B. 19, 1467) and contains sulphur dioxide.

Hydroquinone is dimorphous and crystallizes in monoclinic leaflets and hexagonal prisms. It decomposes when quickly heated. It dissolves readily in water (in 17 parts at 15°), alcohol, and ether. It forms crystalline compounds with H₁S and SO₂; these are decomposed by water. Ammonia colors the aqueous solution reddish-brown. It is only in the presence of ammonia that lead acetate produces a precipitate in the solution of hydroquinone. Oxidizing agents (like ferric chloride) convert hydroquinone into quinone; quinhydrone is an intermediate product.

Hydroquinone, like quinone, forms quinone-dioxime (p. 172) (B. 22, 1283) with hy-

droxylamine hydrochloride.

Hydroquinone is used as a "developer" in photography, and in therapeutics as an

antifermentative and antipyretic agent.

Ethers.—Methylhydroquinone, CH₃. O[4]C₈H₄[1]OH, is formed from methyl arbutin; and from hydroquinone by heating it with caustic potash, and methyl iodide or potassium methyl sulphate (B. 14, 1989). It melts at 53° and boils at 247°. The dimethyl ether melts at 56° and boils at 205°. The ethyl ether melts at 66° and boils at 246°. The diethyl ether melts at 71°.

Hydroquinone bischlorphosphine, C₆H₄(OPCl₂)₂, melts at 65° and boils at 200° (65 mm.), while hydroquinone bisoxychlorphosphine, C₆H₄(OPOCl₂)₂, melts at 123° and

boils at 270° (70 mm.) (B. 27, 2568).

Hydroquinone Diacetate, C₆H₄(O. COCH₂)₃, melts at 123°.

Hydroquinone Dibenzoate, C₆H₄(O. COC₆H₅)₄, melts at 199°.

Homologous Hydroquinones are usually prepared by action of sulphur dioxide upon the homologous quinones. Toluhydroquinone results from the action of hot dilute sulphuric acid upon p-tolylhydroxylamine (p. 70). Hydro-p-xyloquinone bears the name hydrophlorone. Dimethylhydrothymoquinone, boiling at 249°, occurs in the ethereal oil of Arnica montana (A. 170, 363). Ditertiary-amyl-hydroquinone results from hydroquinone and isoamylene with glacial acetic acid and sulphuric acid (B. 25,

```
M. P.
124° (A. 215, 159).
121° (B. 18, 2673).
150° (B. 18, 1151).
                                             212° (A. 215, 169).
                                             169° (B. 18, 1152).
```

Substituted Hydroquinones.—Monochlor- and monobrom-hydroquinones have been obtained by the action of concentrated hydrochloric or hydrobromic acid upon p-quinone (B. 12, 1504). Monochlorquinone gave dichlorquinone, etc. (A. 210, 153). Di-, tri-, and tetrachlorhydroquinones result from the corresponding chlorinated quinone by the action of SO.

Monochlorquinone	melts a	t 104°;	Monobromquinone	melts at	1100.
[2,5]-Dichlorquinone	"	166°;	[2,5]-Dibromquinone	4.6	186°.
[2,6] Dichlorquinone	"	158°;	[2,6] Dibromquinone	"	163°.
Trichlorquinone	44	134°;	Tribromquinone	66	136°.
Tetrachlorquinone	"	232°;	Tetrabromquinone	"	2440.

[1,3]-Dinitro- and [2,5]-dinitrodiethylhydroquinone, melting at 233° and 176° (A. 215, 149), result from the nitration of hydroquinone diethylate and diacetate. change into the same trinitrodiethylhydroquinone, melting at 130°, and [2,5]-dissitrohydroquinone diacetate, melting at 96°. The latter compound exchanges an NO₃-group

Nitrohydroquinone, melting at 133°, is formed in the action of ammonium persulphate upon nitrophenol (J. pr. Ch. [2] 48, 179). Dinitrohydroquinone results from dinitroarbutin and dinitrohydroquinone diacetate. Reduction changes these compounds to amidohydroquinones (B. 22, 1656; 23, 1211). I,4-Diamidohydroquinone is obtained

from the dioxime of 2,5 dioxyquinone (p. 170).

When tetrachlorquinone is digested with a diluted solution of primary sodium sulphite (A. 114, 324) we get dichlorhydroquinone disulphonic acid, C₆Cl₂ { (OH)₂ (SO₂H)₂. Its aqueous solution is colored indigo-blue by ferric chloride. When its alkaline solution is boiled

it oxidizes to potassium enthiochronate (p. 170).

Monthiohydroquinone, C₆H₄[1,4](OH)(SH), melting at 30° and boiling at 167° (45 mm.), results from p-diazophenol chloride and potassium xanthogenate.

Dithiohydroquinone, C_eH₄[1,4](SH)₂, melting at 98°, is obtained from p-benzene disulphonic chloride or diazophenyl disulphide. In the air it gradually oxidizes to p-phenylene disulphonic

phide, $[C_6H_4S_2]x$.

TRIHYDRIC PHENOLS.

The three isomeric trioxybenzenes are known in the compounds pyro-

gallol, phloroglucin, and oxyhydroquinone.

Pyrogallol, Pyrogallic Acid, C₆H₃[1,2,3](OH)₃, melting at 132°, is produced by the elimination of CO₂ from gallic acid or pyrogallocarboxylic acid, CO2H[1]C6H2[3,4,5](OH)3, when heated alone, as was first observed by Scheele (1786), or, better, with water to 210°; also by fusing the two p-chlorphenol-disulphonic acids and hæmatoxylin with potassium hydroxide. It forms white leaflets or needles. It dissolves readily in water, with more difficulty in alcohol and ether. solution absorbs oxygen very energetically (B. 14, 2666), turns brown and decomposes into carbon dioxide, acetic acid, and brown substances. It is used in gas analysis for the determination of oxygen. Pyrogallol quickly reduces salts of mercury, silver, and gold with precipitation of the metals, while it is oxidized to acetic and oxalic acids.

Ferrous sulphate containing ferric oxide colors its solution blue, ferric chloride red. Lead acetate precipitates white, CgH₆O₃. PbO. An iodine solution imparts a purple red color to an aqueous or alcoholic pyrogallol solution. Gallic and tannic acids react similarly.

The dimethyl ether is found in beechwood creosote. It melts at 51-52° and boils at 252° (B. 11, 333). Different oxidizing agents convert it into carulignone, a diphenyl

derivative. The trimethyl ether melts at 47° and boils at 235° (B. 21, 607, 2020). Bromine converts it into xanthogallol, C₁₈H₁₄Br₁₄O₆ (B. 21, R. 626).

The ethyl, diethyl, and triethyl ethers melt at 95°, 79°, and 39°. The syrupy dimethyl acetate yields a quinone, C₆H₂(OCH₃)₂O₂, with chromic acid; the triacetate

crystallizes.

Trichlorpyrogallol, $C_6Cl_3(OH)_3$, melts with decomposition at 177° (B. 20, 2035).

Trichlorpyrogallol, $C_6Bl_3(OH)_3$, from pyrogallol and bromine, when digested with bromine yields xanthogallol, $C_{18}Il_4Bl_{14}O_6$, melting at 122° (A. 245, 335). Methylpyrogalloldimethyl ether, $CH_3 \cdot C_6Il_2(OH)(OCH_3)_3$, melting at 36° and boiling at 265°, occurs in beechwood creosote (B. 12, 1371). Methyl-[3,4,5]-pyrogallol-[4,5]-dimethyl Ether, Iridol, melting at 57° and boiling at 249°, is formed on distilling iridic acid, CO. H. C. H. (OH)(OCH), (B. 25, 2018). CO₂H . CH₂ . C_aH₂(OH)(OCH₃)₂ (B. 26, 2018).

Propylpyrogallol-dimethyl Ether, Picamar, C₂H₁, C₄H₂(OH)(OCH₂)₂, boiling at 245°, was discovered in beechwood creosote by Reichenbach (B. 11, 329).

Phloroglucin, CaH3[1,3,5](OH)3, melts at 218° when it is rapidly heated. Hlasiwetz first obtained it (1855) in the decomposition of phloretine (see this). It can also be prepared from quercetine, hesperidine, and other glucosides (see these). It is formed from different resins (catechu, kino, dragon's blood, and others), on fusion with caustic potash. It is most easily made by fusing resorcinol with caustic soda (B. 14, 954; 18, 1323); by the fusion of orcin and benzene trisulphonic acid with sodium hydroxide; also by the saponification and decomposition of synthetically prepared phloroglucin-

tricarboxylic ester, which gives up 3CO₂ (B. 18, 3454).

It crystallizes in large, colorless prisms with 2H₂O; these effloresce in the air. It loses all its water of crystallization at 110°, melts at 218°, and sublimes without decomposition. It has a sweetish taste, and dissolves readily in water, alcohol, and ether.

Lead acetate does precipitate it; ferric chloride colors its solution a dark violet.

Chlorine oxidizes phloroglucin to dichloracetic acid and tetrachloracetone (p. 46). One of the first intermediate products is hexachlor triketo-R-hexylene (p. 46). For the action of bromine see B. 23, 1706. It is converted by reduction into phloroglucite or sym.-trioxyhexamethylene (B. 27, 357).

Phloroglucin, in most of its reactions,—for example, with phenylcyanate (see B. 23, 269),—conducts itself like a trihydric phenol, C_eH₃(OH)₃; on the other hand it unites with three molecules of hydroxylamine to form a trioxime (see below), hence it may be considered a triketone-[1,3,5]-triketo-hexamethylene (B. 19, 159):

In order to explain the trioxime formation it might be assumed that the [1,3,5]-trioxybenzene formula is the unstable pseudo-form (1, 54) of phloroglucin. This assumption is, however, not necessary. It might be imagined, too, that hydroxylamine first attaches itself to the double union of the trioxybenzene ring, and then the splitting of

the three molecules of water took place.

Normal Phloroglucin Ethers.—The trimethyl ether, melting at 52° and boiling at 255°, Normal Phloroglucin Ethers.—The trimethyl ether, melting at 52° and boiling at 255°, and the triethyl ether, melting at 43°, are formed upon heating the alcoholic solutions of phloroglucin with HCl, and then with methyl iodide and caustic potash (B. 21, 603). The trimethyl ether also results from the action of caustic potash upon methyl hydrocotoine (B. 26, 784). Phloroglucintriacetate melts at 105°. See B. 28, 24; 29, R. 990, for the action of phloroglucin upon the sugars. Nitrosophloroglucindiethyl Ethers: diethoxyquinoxime, $C_8H_2(OC_2H_6)_2(NO)(OH)$, a-body melting at 117°, β -variety at 192-195° with decomposition—see B. 29, R. 849. Trinitrosophloroglucin, $C_8(NO)_3(OH)_3$, (B. 11, 1375). Trinitrophloroglucin, $C_8(NO_3)_3(OH)_3$. Triamidophloroglucin, $C_8(NH_2)_3(OH)_3$, yields croconic acid when boiled with MnO₃ and soda (B. 26, 2185). When phloroglucin is treated with methyl iodide and alcoholic potash the final product is Hexamethylohloroglucin or hexamethyltriktohexamethylene. $C_8(CH)_3(OH)_3$, melting

is Hexamethylphloroglucin or hexamethyltriketohexamethylene, C₆(CH₃)₆O₃, melting at 80° and boiling at 248°. Fuming hydrochloric acid decomposes it into di isopropyl

Phloroglucin Trioxime, C₆H₆(NOH)₈, is a crystalline powder exploding at 155°. Phenyl hydrazine adds itself to phloroglucin just as it does to oxalo-acetic ester and dioxysuccinic ester (p. 123).

Oxyhydroquinones result from the reduction of oxyquinones.

Oxyhydroquinone, C₆H₃[1,2,4](OH)₃, is produced on fusing hydroquinone with KOH (together with tetra- and hexaoxy diphenyl (B. 18, R. 24). It is crystalline, very soluble in water and ether, and in aqueous solution soon acquires a dark color. It melts at 140.5°. Ferric chloride colors it a dark greenish brown. Its tri-ethyl ether, $C_aH_a(O. C_2H_5)_a$, is obtained from trioxyethyl benzoic acid (from sesculetin). It can also be prepared by ethylating ethoxy-hydroquinone. It melts at 34° (B. 20, 1133). The trimethyl ether, $C_6H_3(O \cdot CH_3)_3$, from methoxy-quinone (p. 170), boils at 247°.

TETRAHYDRIC PHENOLS.

There are three possible isomerides; the symmetrical and unsymmetrical varieties are known in a free state, while the third member has been liberated in the form of simple ethers from various plant substances.

(1) Apionol, v-Tetraoxybenzene, [Phentetrol], has been obtained as Dimethyl Apionol, $C_6H_5[1,2,3,4](O\cdot CH_3)_3(OH)_3$, by heating apiolic acid with caustic potash. It melts at 100° and boils at 298° . Tetramethyl Apionol, $C_6H_2(O\cdot CH_3)_4$, melts at 81° . [1,2]-Methylene-3,4-dimethyl Apionol, $C_6H_2(O_2\cdot CH_3)(O\cdot CH_3)_3$, Apione, is formed when apiolic acid is heated with dilute sulphuric acid. It melts at 69° (B. 24, 2608; 29, 1806).

I-n-Propyl-2,3,4,5-tetraoxybenzene is obtained as methylene dimethyl ether dihy-

droapiol, melting at 25° and boiling at 292°, in the reduction of isapiol.

(2) Unsym. Tetraoxybensene, C₆H₂[1,2,3,5](OH)₄, is an amorphous, glassy mass obtained from iretol by the action of hydrochloric acid at 150°. The 1,3 dimethyl ether is prepared by reducing 1,3-dimethoxy-2,5-quinone. It melts at 158°. The tetramethyl ether melts at 47° and boils at 271° (B. 23, 2291).

Iretol, CH₃O. C₆H₃(OH)₃, melting at 186°, is one of its monomethyl ethers. It is

formed together with iridic acid on fusing trigenin with potash (B. 26, 2015).

(3) Symmetrical Tetraoxy-benzene, C₂H₂[1,2,4,5](OH)₄, is obtained by reducing 1,4-dioxy-2,5-quinone with stannous chloride. It melts at 215-220°. Its tetra-acetylester melts at 217° (B. 21, 3374).

Dichlortetraoxy-benzene, hydrochloranilic acid, CaCla (OH)4, results in the reduc-

tion of chloranilic acid (p. 170) with sulphurous acid (A. 146, 32).

Amido-s- Tetraoxybenzene results from the action of stannous chloride upon nitrodioxyquinone, and also Nitroamido-s-tetra-oxybenzene and Diamido-s-tetraoxy-benzene (B. 18, 502), by the reduction of nitranilic acid. Croconic acid (p. 171) and ammonia are produced on boiling the diamido-body with potash; oxidizing agents convert it into diamido dioxy quinone.

Hydroeuthiochronic alkali salts—see euthiochronic acid, p. 170.

Pentahydric Phenols are not known. Quercite, which will be discussed in connection

with the cyclohexane derivatives, is pentoxyhexahydrobenzene.

Hexahydric Phenols.—In describing the benzene ring formations (p. 42) mention was made of the remarkable isolation of potassium hexaoxybenzene or potassium carbon monoxide (discovered by Liebig in 1834), which results upon conducting carbon monoxide over heated potassium (confirmed by Nietzki and Benkiser in 1885). Dilute hydrochloric acid, acting upon the fresh mass, yields hexaoxybenzene.

Hexaoxybenzene, C₆(OII)₆, is obtained from triquinoyl (p. 171) by reduction with stannous chloride and hydrochloric acid. It separates in the form of small, grayish-white needles, which acquire a reddish-violet color on exposure to the air. They are not fusible, but decompose at about 200°. Concentrated nitric acid oxidizes it to tri-

quinoyl.

It forms the hexacetyl derivative, C₆(O. C₂H₃O)₆, when heated with acetic acid and sodium acetate. It is a crystalline mass, melting at 203° (B. 18, 506).

8. QUINONES.

This is the designation ascribed to all derivatives of benzene in which 2II-atoms are replaced by 2O-atoms. The replacement is either in the o- or the p-position. We distinguish ortho-quinones and para-quinones. The latter are especially characteristic of the mono-nucleus aromatic hydrocarbons. Metaquinones are not known.

ORTHOQUINONES.

In this series belong the tetrahaloid substitution products of o-benzoquinone, not known in the free condition: Tetrachlor-o-bensoquinone, C₆Cl₄[1,2]O₂, melting at 131°, and Tetrabrom-o-bensoquinone, C₆Br₄[1,2]O₂, melting at 150°. They are produced when chlorine or bromine acts upon pyrocatechin dissolved in glacial acetic acid (Zincke, B. 20, 1776).

Homologous orthoquinones are produced by the action of chlorine upon the corresponding orthodiamine hydrochlorides. The o-diketochlorides are the first products, but they can be reduced to chlorinated o-dioxybenzenes, which yield the chlorinated o-quinones upon oxidation (B. 27, 560).

PARAQUINONES.

The constitution of the *true quinones* or *paraquinones* of the aromatic hydrocarbons having one nucleus is not fully established. They are considered either as benzene derivatives, the oxygen atoms being assumed to be linked to one another, or as p-dihydrobenzene derivatives, containing two ketone-groups.

The first view compares the paraquinones to peroxides; they are indeed powerful oxidizing agents. Upon reduction they do not become the p-diglycols of the p-dihydrobenzenes, but p-dioxybenzenes, so-called hydroquinones, which are true benzene derivatives. Further, each oxygen atom, by the action of PCl₅, is replaced by one chlorine atom. In opposition to the peroxide formula of the paraquinones we have the p-diketone formula, in support of which we can bring forward the formation of a monoxime and a dioxime, as well as the absorption of 2Br and 4Br by paraquinone (J. pr. Ch. [2] 42, 61; B. 23, 3141). Nitrosophenol is considered by most chemists to be quinone-monoxime. Phenylhydrazones of the p-quinones have not been obtained, because the latter bodies oxidize phenylhydrazine (p. 173). The various formulas for ordinary quinone and its oximes are:

Quinone, Benzoquinone, C₆H₆O₂, melting at 116°, was first obtained in 1838 by Woskresensky upon oxidizing quinic acid, a hexahydrotetra-oxybenzoic acid, with manganese peroxide and sulphuric acid. Woskresensky named the new body Quinoyl, while Berzelius (Berz. Jahresb. 19, 407) proposed the name Quinone.

Quinone is made from hydroquinone or p-dioxybenzene (p. 162) by

the action of ferric chloride, and from many p-diderivatives of benzene by oxidation, mostly with potassium bichromate and sulphuric acid; thus, from p-phenylenediamine, sulphanilic acid, p-amidoazobenzene, p-amidophenol, p-phenolsulphonic acid, p-diamidodiphenyl, or benzidine. It is usually prepared by oxidizing aniline with sodium bichromate and sulphuric acid (Nietzki, B. 20, 2283). It has also been obtained by oxidizing quinite (see this).

Quinone crystallizes in golden-yellow prisms. It possesses a peculiar, penetrating odor. It attacks the skin. It distils readily with steam, and dissolves easily in hot water, alcohol, and ether. It turns brown on exposure to sunlight. In the presence of the latter it combines to diexybenzophenones with benzaldehyde (1, 75). Reducing agents (SO₂, Zn, and HCl) convert it first into quinhydrone, an addition-product of quinone and hydroquinone, which nascent hydrogen changes into hydroquinone.

Other phenols readily add themselves to quinone (below). Concentrated airic acid dissolves it in the cold, but when the acid is hot it is decomposed, oxalic and prussic acids being formed. Bromine converts quinone into quinone di- and tetrabromides, melting at 80° and at 170–175°. p-Diketohexamethylene, the hydride corresponding to quinone tetrabromide, has been obtained by starting with succino-succinic ester.

Phosphorus pentachloride converts quinone into p-dichlorbenzene (p. 59), hydroxylamine chloride changes it to quinone-oxime or nitrosophenol (p. 152), and quinone-dioxime. Phenylhydrazine reduces it to hydroquinone; a-alkylphenylhydrazines show a similar reducing power, changing simultaneously with tetrazones (p. 131). a-Acidylphenylhydrazines, on the other hand, yield monohydrazines of the quinones (p. 172). Aniline combines with quinone, forming dianilidoquinone, dianilidoquinone-anil, and dianilidoquinone-dianil. For the condensations of quinones with acetoacetic ester to form cumarenes, see the latter.

Quinone Phenol Addition-Products (A. 215, 134).—Phenoquinone, C₆H₅O₃.- 2C₆H₅OH, melting at 71°, is formed on adding quinone to phenol. It is very volatile. It crystallizes in red needles, which are turned blue by caustic potash, and green by barium hydroxide.

Quinhydrone, $C_6 \Pi_4 O_2$. $C_6 \Pi_4 (O \Pi)_2$.—This is produced by the direct union of quinone with hydroquinone. It appears as an intermediate product in the reduction of quinone or in the oxidation of hydroquinone,—e. g., in electrolysis (B. 29, R. 1122),—and is changed by continued oxidation into quinone, and by reduction into hydroquinone. It consists of green prisms or leaflets with metallic lustre, has a quinone-like odor, melts readily, and dissolves in hot water with a brown, in alcohol and ether with a green, color. When it is boiled with water it decomposes into hydroquinone and quinone. The constitution of these compounds probably corresponds to the following formulas (B. 28, 1615; 29, R. 903):

Homologous p-Quinones.—They are produced (1) by the oxidation of the corresponding p-dioxybenzenes or hydroquinones (even with ferric chloride), of the corresponding p-diamines, p-amidophenols, such as amidothymol and many other disubstitution-products belonging to the p-series, with ferric chloride, chromic acid, and manganese dioxide and sulphuric acid. (2) Even mono-substituted alkyl benzenes yield p-quinones, especially when they are oxidized with chromic acid. This is particularly true of amido-and oxyalkyl benzenes or alkyl phenols. Thus, o toluidine yields toluquinone, while

thymol and carvaerol yield thymoquinone, or thymoll. Frequently an alkyl-group will be displaced, favoring the p-quinone formation, and be substituted by oxygen—e. g., in the oxidation of amidomesitylene (B. 18, 1150)—to m-xyloquinone and of pseudocumidine to p-xyloquinone. (3) p-Xyloquinone and duroquinone have been synthesized by the action of caustic potash upon the aliphatic a-diketones—diacetyl and acetyl propionyl (1, 322; 11, 42). In this reaction quinogens are first produced, afterward follow the p-quinones:

p-Xyloquinone or phlorone occurs in the tar of beechwood.

Properties.—The homologous p-quinones are very similar to their prototype—benzoquinone. They are also yellow-colored, possess an odor similar to that of quinone, sublime readily, and behave chemically like p-benzoquinone. They form quinhydrones (p. 168), are easily reduced by sulphurous acid to p-hydroquinones (p. 162), and combine to nitrosophenols (p. 152) and quinone-dioximes (p. 172) with hydroxylamine.

Toluquinone, o-Xyloquinone,		M. P. 67° 55°
m-Xyloquinone,	(CH ₃) ₂ [1,3]C ₆ H ₂ [2,5]O ₃	102° 123°
o-Ethylbenzoquinone,	$(C_3H_5)[2]C_6H_3[1,4]O_5$	38° (B. 28, R. 471). 11° (B. 27, 1430).
Pseudocumoquinone,	(CH ₈), [1,2,4,5]C ₆ [3,6]O ₃	111° (B. 29, 2171).
Thymoquinone,	$(CH_3)(C_3H_7)[1,4]C_6H_3[2,5]O_3$	45°, B. P., 232°.

When an ethereal solution of thymoquinone is allowed to stand in sunlight for some time, polythymoquinone, melting at 200°, separates (B. 18, 3195). See B. 29, 2176 for diduroquinone.

Quinone Haloids are obtained by the substitution of quinones or by the oxidation

of substituted hydroquinones (p. 162).

A mixture of tri- and tetrachlorquinone, called chloranil, consists of bright-yellow leaflets. It is obtained from many benzene compounds (aniline, phenol, isatin) by the action of chlorine or potassium chlorate and hydrochloric acid (B. 29, R. 236). It oxidizes and serves as an oxidizing agent in the manufacture of coloring matters.

Trichlor- and tetrachlorquinone are separated from one another by the insolubility of the latter in water. The chlorquinones are obtained from chlorhydroquinones by oxida-

tion with nitric acid (A. 146, 9; 210, 145; 234, 14):

Monochlorquinone, [2,5].Dichlorquinone, [2,6].Dichlorquinone, Trichlorquinone s.	159°; 120°; 166°;	Monobromquinone, [2,5]-Dibromquinone, Tribromquinone, Tetrabromquinone s	• •	18	88°. 22°.
remachioidamone s	uomines.	renamoniquinone a	uom	ucs.	

PCl₅ converts tetrachlorquinone into phosphorus-containing derivatives, C₆Cl₅. OPO-Cl₂ (?), and then into hexachlorbenzene (p. 59) (B. 24, 927). It absorbs two atoms of chlorine and becomes hexachlor-p-diketo-R-hexene (p. 45), which caustic soda resolves into dichlormaleIc acid and trichlorethylene. Potassium hydroxide converts trichlorquinone and tetrachlorquinone into potassium chloranilate (p. 170), and tribrom- and tetra-bromquinone into potassium bromanilate.

Nitroquinone, NO₂C₆H₂O₂, decomposing at 206°, consists of yellow glistening crystals, and is formed by oxidizing 2-nitro-p-amidophenol, NO₂[2]C₆H₃[4]NH₂[1]OH, with potassium dichromate and sulphuric acid. It is very sparingly soluble in water, not volatile with aqueous vapor, and dissolves with difficulty in ether, and very readily in alcohol and in chloroform. It imparts a black color to the skin (B. 28, 1386).

170

Amidoquinones.—Chloranilamide, C₆Cl₂(NH₂)₂O₂, is obtained from chloranilic acid. Aniline, acting upon a hot alcoholic solution of quinone, produces not only hydroquinone, but also dianilidoquinone, dianilidoquinone-anil, and -dianil (p. 173), as well as 2,5-dioxy-1,4-quinone (below).

OXYQUINONES AND POLYQUINOYLS.

Bensene Oxyquinones.—Methoxyquinone, CH₂O[2]C₂H₂: O₂, melting at 140°, is produced by oxidizing o-amidoanisol, C₄H₄(NH₂). O. CH₃, with chromic acid.

Chloranilamic Acid, C₆Cl₂(NH₂)(OH)O₂, is obtained from chloranil.

2,6-Dimethoxyquinone, (CH₂O)₂[2,6]C₂H₂O₃, melting at 240°, results from the oxidation of timetholypergallol and trimethyliphersyllable.

tion of trimethylpyrogallol and trimethylphloroglucin (p. 165) (B. 26, 784).

2,5 Dioxyquinone, (HO)₂[2.5]C₈H₂O₂, is obtained from dioxyquinone dicarboxylicatid (see this) by boiling with hydrochloric acid, by the oxidation of diamido-resorcin (B. 21, 2374; 22, 1285), and by the action of dilute sulphuric acid upon dianilidoquinous (B. 23, 904). It separates in small blackish-brown crystals, which sublime above 185°. Stannous chloride reduces it to symmetrical tetraoxybenzene (p. 166), and dianilidoquinone is produced when it is heated with aniline. Substitution-products of 2,5-dioxyquinone have been obtained from tetrachlor- and tetrabromquinone as starting-out substances. Two of their halogen atoms are exchanged with extreme ease.

Chloranilic Acid, $C_0C_1(OH)_2O_3$, reddish, shining scales, is separated by acids from potassium chloranilate, $C_0C_1(OK)_2O_3 + H_2O$, which crystallizes in dark-red needles, dissolving with difficulty in water. Potassium chloranilate is produced as well from tri- as from tetrachlorquinone by the action of caustic potash. Hypochlorous acid or chlorine acting upon chloranilic acid, produces tri- or tetrachlortetraketohexamethylene, which change quite readily with the intermediate production of unstable oxyacids into

trichlor- and tetrachlortriketopentamethylene (B. 25, 827, 842).

Bromanilic Acid, C₆Br₂(OH)₂O₂, corresponds to chloranilic acid and with bromine yields similar transposition-products to those obtained from it by the action of chlorine.

Nitranilic Acid, $C_6(NO_2)_2O_2(OII)_2$.—It crystallizes with water in golden-yellow needles or plates, melts in its water of crystallization, becomes anhydrous at 100°, and detonates at 170° without melting. It is formed from quinone and hydroquinone with nitrous acid, and from terephthalic and dioxyquinone-terephthalic acids by the action of When nitroanilic acid is reduced, it yields diamidotetraoxybenzene fuming nitric acid. (p. 166), which renders possible the transition from chloranil to triquinoyl (see below), and potassium hexaoxybenzene.

Amidoanilic Acid, Diamidodioxyquinone, C6(NH2)2(OH)2O2, reddish-blue needles,

formed from diamidotetraoxybenzene by oxidation in the air or by nitrous acid.

Potassium Euthiochronate, C₆(SO₃K)₂(OH)₂O₂, see dichlorhydroquinone-disulphonic

acid (p. 164).

Tetraoxyquinone, C₆(O₂)(OH)₄, formerly called dihydrocarboxylic acid, is obtained by oxidizing the aqueous solution of hexaoxybenzene by exposure to the air (B. 18, 507, 1837). It may also be obtained from diamido-dioxyquinone by boiling with hydrochloric acid, as well as by the action of concentrated nitric acid upon inosite. Metallic black

needles, with a green, metallic reflex. It is a strong dibasic acid.

Homologous Oxyquinones result upon treating haloid quinone homologues with caustic potash, and on heating amido or anilidoquinones with alcoholic hydrochloric acid or sulphuric acid. Dianilidotoluquinone, melting at 232°, yields anilido-oxytoluquinone, decomposing at 250°, and dioxytoluquinone, CH₃. C₆H(OH)₂O₂, melting at 177° (B. 16, 1559). Oxythymoquinone, (C₃H₇)(CH₃)C₆H(OH): O₂, melting at 166°, is obtained from brom- or methylamidothymoquinone. Dioxythymoquinone melts at 213° (B. 14,

It is also very probable that pipitzahoic acid, C15H19(OH): O2, found in the root of Trixis pipitzahuac and melting at 103°, belongs to the oxyquinones, containing but one nucleus. It recalls, by its behavior, oxythymoquinone. Oxypipitzahole Acid, C. H18:

 $C_6(OH)_2: O_2$ (?), melts at 138° (A. 237, 90).

Polyquinoyl Compounds.—As mentioned under benzoquinone (p. 167), Woskresensky originally called this compound quinoyl. Nietzki and Benckiser introduced this ame in a different sense. They applied it to the quinone group O2, when they disovered dioxydiquinoylbenzene and triquinoylbenzene to be bodies containing more han one quinone-group O2. For simplicity's sake they abridged these names to dioxy-

tiquinoy! and triquinoy!.

Dioxydiquinoyl, C₆(O₃)(O₂)(OH)₃, called *rhodisonic* acid, is prepared by reducing triquinoyl with aqueous sulphurous acid (B. 18, 513). It consists of colorless leaflets, very readily soluble in water. It decomposes quite rapidly in aqueous solution. The polassium sall, C₆O₄(OK)₃, may be obtained by treating the acid with potashes, and also by washing potassium-hexaoxybenzene (potassium carbon monoxide, p. 166) with alcohol. It forms dark-blue needles, dissolving in water with an intense yellow color (B. 18, 1838).

Consult B. 23, 3140, for the constitution of rhodizonic acid.

Triquinoyl, C.O. + 8H.O. is probably hexaketo-hexamethylene (B. 20, 322). It results upon oxidizing dioxydiquinoyl and diamidotetraoxybenzene (p. 166) with nitric acid. It is a white, micro-crystalline powder (B. 18, 504). It melts about 95°, giving up water and CO₂. It is likewise decomposed by warming it with water to 90°. Stannous chloride reduces it to hexaoxybenzene, which is oxidized in alkaline solution to tetraoxyquinone, C₈(O₂)(OH)₄ (see above).

Nietzki and Benckiser (1885) discovered the relations existing between potassium carbon monoxide and phenol. Compare the following:

Addendum. - Pentacarbocyclic compounds are readily formed from triquinoyl and dioxydiquinoyl, as well as from some hexa-substitution derivatives of benzene, from which these polyquinoyl bodies arise—e.g., hexaoxybenzene, diamidotetraoxybenzene,

croconic Acid Hydride, C₆H₄O₆, is formed upon treating rhodizonic acid with excessive alkali, or croconic acid with hydriodic acid. It is distinguished by its barium salt, C₃H₂BaO₆ + 2H₂O. Its formation is probably due to the breaking down of an unstable oxyacid, produced by the action of the caustic alkali upon two of the combined COgroups of the rhodizonic acid (see the rearrangement of benzilic acid, 1, 54):

$$\begin{array}{c} \text{HO.C.CO.CO} \\ \text{HO.C.CO.CO} \\ \text{HO.C.CO.CO} \\ \text{CO.CO} \\$$

Croconic Acid, C₅O₂(OH)₂ + 3H₂O, consists of sulphur-yellow leaflets; it loses its water of crystallization at 100°. It dissolves very readily in water and alcohol, and is produced by the alkaline oxidation of most of the hexa-substituted benzene-derivativesc. g., hexaoxybenzene, dioxydiquinoyl, diamidotetraoxybenzene, etc. The hydride of croconic acid is an intermediate product, which changes quite readily to the acid. Triquinoyl, when boiled with water, decomposes into carbon dioxide and croconic acid:

$$C_6O_6 + H_2O = C_5H_2O_5 + CO_2$$

Its potassium salt, C₆O₆K₂ + 3H₂O, crystallizes in orange-yellow needles; hence the name from κρόκος, safran (Gmelin, 1825). When oxidized with nitric acid or chlorine

Leuconic Acid, C₂O₅ + 4H₂O, Pentaketocyclopentane, which is reconverted into croconic acid by sulphur dioxide. This acid bears the same relation to croconic acid

that rhodizonic acid sustains to triquinoyl. It is very soluble in water, but dissolves with difficulty in alcohol and ether. It crystallizes in small colorless needles. The pentaoxime, C₃(:N.OH)₆, decomposing at 172°, is isomeric with fulminic acid, cyanic acid, cyanuric acid, and by reduction yields penta-amido-pentol, CaH(NH2), penta-amidocyclopentadiën (see p. 25) (B. 22, 916).

QUINONE NITROGEN DERIVATIVES.

The quinone oxygen atoms can be replaced by N(OH), NCI, NII, NC₂H₂, and similar

Quinone Dioximes.—In connection with the p-nitrosophenols (p. 152), and in the explanation of Fittig's diketone formula for p-quinone, it was indicated that many chemists regarded the p-nitrosophenols, resulting from the action of hydroxylamine hydrochloride upon the p-quinones, as monoximes of the latter. Indeed, the p-nitrosophenols, by action of hydroxylamine hydrochloride, change to p-quinonedioximes. It is true these two classes can be viewed as constituted according to the peroxide formula of the p-quinones. Their dioximes unite with acetic anhydride to diacetyl compounds. p-Dinitrosobenzenes are produced by the oxidation of their alkaline solutions (also on exposure to the air). Nitric acid oxidizes them to p-dinitrobenzenes (B. 21, 428).

p. Quinone Dioxime, C₆II₄(N. OII)₂, consists of colorless or yellow needles, which decompose at 240°. Toluquinone Dioxime explodes at 220° (B. 21,679). p. Xyloqui none Dioxime melts about 272° (B. 20, 978). Dinitroresorcinol and hydroxylamine yield diquinoyltrioxime, C₈H₂O(NOH)₃, and diquinoyltrioxime, C₆H₂(NOH)₄ (B. 30, 181). Quinone-chlorimides.—We must regard them either as diketones or peroxides, in which oxygen is replaced by the group NCl. The latter view corresponds to the

formulas:

They are produced from p-amidophenols and p-phenylenediamines (their HCl-salts) by oxidation with an aqueous solution of bleaching lime. They revert to p-amidophenols or p-phenylenediamines upon reduction. The monochlorimides form the indophenol dyestuffs (p. 173) with phenols and tertiary anilines.

Quinone-chlorimide, O[1]C₆H₄[4]NCl, forms golden-yellow crystals, which melt at 85°, volatilize readily with steam and smell like quinone. It is easily soluble in hot water, alcohol, and ether. When boiled with water it decomposes into NH4Cl and quinone (J. pr. Ch. [2] 23, 435).

Quinone-dichlorimide, C₆H₄[1,4](N₂Cl₂), crystallizes in needles which deflagrate

at 124° (B. 12, 47).

Trichlor-quinone-chlorimide melts at 118° (J. pr. Ch. [2] 24, 429). Dibrom-quinone-chlorimide melts at 80° (B. 16, 2845).

Quinone Phenylhydrazones. - While phenylhydrazine and alkylic phenylhydrazines are oxidized by quinone, a benzoylphenylhydrazine and quinone yield Quinone benzoylphenylhydrazone, $C_6H_4(O)$: $NN(CO \cdot C_6H_6)C_6H_5$, melting at 171°. Alkali or sulphuric acid readily decomposes it into benzoic acid and p-oxyazobenzene, which yields the isomeric p-benzoxyazobenzene, $C_6H_6CO \cdot OC_6H_4N_3C_6H_6$, upon introducing the benzoyl group. The o-azophenols are very probably hydrazones of o-quinones (p. 156 and B. 28, 2415).

Quinone-imides .- Quinoanils: Diamidoquinone-imide, (NH2)2C8H2(O)(NH), or amidodiimidophenol, (HO)(NH2)C6H2(NH)2, is made from triamidophenol (A. 215,

351).

Quinone Phenylimide, Quinone Monanil, C6H4 O O C6H4 N. C6H5 melting at 97°, consists of fiery-red crystals. It is formed upon oxidizing p-oxydiphenylamine in benzene solution with mercuric oxide, and upon reduction reverts to the same (B. 21, R. 434).

Diphenyl-p-ezophenylene, Quinone Dianil, CaH, N. CaH, or CaH, N. CaH, melting at 1760-1800, results from the oxidation of diphenylamine (p. 80), and diphenylp-phenylenediamine (B. 21, R. 656). Reduction converts quinonedianil into diphenylp-phenylenediamine. Both anils sustain the same relation to the corresponding diphenylamine-derivatives that quinone bears to hydroquinone:

$$\begin{array}{lll} C_{e}H_{4} {<} & C_{b} \\ C_{e}H_{4} {<} & C_{b} \\ C_{e}H_{4} {<} & C_{b}H_{6} \\ C_{e}H_{6} {<} \\ C_{e}H_{6} {<} & C_{b}H_{6} \\ C_{e}H_{6} {<} \\$$

Two phenylamido-groups can be as readily introduced into the benzene residue of quinone-anil and quinone-dianil as into quinone itself, from which, on boiling its alcoholic soluone-anil and quinone-dianil as into quinone itsell, from which, on dolling its alcoholic solution with aniline, dianilidoquinone (together with hydroquinone) results. In the presence of acetic acid the product is dianilidoquinone-anil, $(C_6H_5NH)_2C_6H_4(O)(NC_6H_5)$, melting at 202°; brown-red needles. It is also formed upon digesting quinone-monanil (together with p-oxydiphenylamine, B. 21, R. 656) with aniline, and when aniline is oxidized with hydrogen peroxide in a feebly acid solution (B. 25, 3574).

Dianilidoquinone-dianil, Azophenine, $(C_6H_5NH)_2C_6H_2(NC_6H_6)_2$, melting at 241°, consists of garnet-red leaflets. It is produced (1) by digesting quinone-dianil with aniline ddiphenyl-n-phenylenediamine is formed at the same time, B. 21, R. 656): (2) by fusing

(diphenyl-p-phenylenediamine is formed at the same time, B. 21, R. 656); (2) by fusing quinone with aniline and aniline hydrochloride (B. 21, R. 683); (3) by the action of aniline upon amidoazobenzene, p-nitrosophenol, and p-nitrosodiphenylamine (B. 20, 2480). It changes to fluorindin when heated (B. 23, 2791).

The quinone-anils are important intermediate products in the formation of the *induline*

dyes (see these) (B. 25, 2731; A. 262, 247).

Indophenols and Indoanilines.—These compounds are obtained from quinonemonoanil or quinone-phenylimide by replacing the p-hydrogen atom of the anil-group by an OH- or an NH₂-group. They are dyes. Like many members of this class, they are decolorized by the addition of hydrogen. The resulting bodies are leuco-compounds, p-disubstituted diphenylamines. (Nomenclature, B. 29, R. 94.)

Indophenols are produced (1) by allowing the quinone-chlorimides to act upon phenols; (2) by oxidizing a mixture of a p-amidophenol and phenol. They dissolve in alcohol with a red color, and possess a phenol-like character. Their salts with the alkalies and ammonia dissolve in water with a blue color.

Quinone-phenolimide, $C_6H_4 < \bigcup_{i=1}^{N} C_6H_4$, also results upon heating phenol-

blue with soda-lye (B. 18, 2916), but owing to its instability, cannot be obtained in a free condition. By reduction it changes to colorless p-dioxydiphenylamine. Dibrom-quinone-phenolimide, C₆H₂Br₂< N. C₆H₄OH, from dibromquinone-chlorimide, is

from dibromquinone-chlorimide, is

more stable than quinone-phenolimide. Free dibromphenolimide crystallizes in darkred prisms having a metallic lustre; they dissolve in alcohol and ether with a fuchsinered color. Strong mineral acids decompose it into dibromphenol and quinone.

The Indoanilines are produced (1) by the action of quinone chlorimide upon dimethyl aniline in alcoholic solution; (2) by the action of nitroso- and nitro-dimethylaniline upon phenol in alkaline solution, especially in the presence of reducing agents (Witt, 1879); (3) by the oxidation in alkaline solution (with sodium hypochlorite) of a mixture of a p-phenylenediamine with a phenol, or of a p-amidophenol with a primary monamine.

The indoanilines are feeble bases. They are rather stable toward the alkalies; acids quickly decompose them into quinones and the p-phenylenediamines. They are changed to the leuco-compounds: amido-oxy-diphenylamines, by reduction (absorption of two hydrogen atoms); these dissolve readily in alkalies, and are readily reconverted (oxidized) into indoanilines (by exposure of their alkaline solution to the air). The free indoanilines have a deep-blue color, and can be applied as dyestuffs. For this purpose

they are converted into their alkaline leuco-derivatives, which are soluble, and the material is impregnated or printed with these. Oxidation (by exposure to the air or with $K_3Cr_3O_7$) develops the color. The simplest aniline is Quinone Anilinimide, $N \cdot C_6H_4 \cdot NH_3$, a violet dye, formed by the oxidation of p-phenylene diamine, $C_gH_4(NH_2)_3$, with phenol. Quinone-dimethyl-anilinimide (phenol blue), $C_gH_4 < \frac{N}{L}$. $C_gH_4 \cdot \frac{N(CH_3)_2}{L}$, results from unsym.-dimethyl-p-phenylenediamine and

phenol. It has a greenish-blue color and dissolves in acids with a blue color. boiled with soda-lye it splits off dimethylamine and becomes quinone-phenolimide. Sulphuric acid decomposes it into quinone and dimethyl-p-phenylenediamine. general reaction, hence can be used opportunely for the preparation of quinones (B. 28,

R. 471; 29, R. 24).
Indamines.—These are derived from the indoanilines by the replacement of the quinone-oxygen atom by the imido- or alkylimido-group. They are therefore derivatives of the unknown quinone diimide, and bear an intimate relation to p-diamidodiphenylamine, which is formed by the reduction of the simplest indamine and is the leuco-deriva-

tive of the latter.

The Indamines arise (1) by oxidation, in neutral solution and in the cold, of a mixture of a p-phenylenediamine with an aniline (Nietzki), or (2) by the action of nitrosodimethyl aniline upon anilines or m-diamines (Witt). They are feeble bases, forming blueor green-colored salts with acids, but with an excess of the latter are very easily split up into quinone and the diamine. Because of their instability they find no application, and are only important as intermediate products in the manufacture of thionine and safranine dyestuffs (into which they can be readily transposed). For the relations of the indophenols, indanilines, and indamines to the dyes of the oxazine-, thiazine-, and diazineseries—e. g., resorufin, methylene blue—the indulines and safranines, see the latter. The simplest indamine is-

Phenylene Blue, $C_6 II_4 < N \cdot C_6 II_4 NH_2$ or $N < C_6 H_4 NII_2$ $C_6 H_4 = NH$ This is produced by

the oxidation of p-phenylenediamine with aniline. Its salts are greenish-blue in color. It yields diamido-diphenylamine by reduction. Its tetramethyl-derivative is—

Dimethylphenylene Green, $N < \frac{C_0}{C_0}H_4 \cdot \frac{N(CH_3)_2}{N(CH_3)_2}Cl$ (Bindschedler's green). This

is obtained by oxidizing dimethyl paraphenylenediamine with dimethyl aniline. Its salts dissolve in water with a beautiful green color. Its reduction yields tetramethyldiamido-diphenylamine. Digestion with dilute acids resolves it into quinone and dimethylamine (B. 16, 865; 17, 223). On standing with soda-lye, dimethylamine splits off and phenol blue is produced; this further separates into quinone phenolimide (p. 173) (B. 18, 2915).

Toluylene Blue, $N < C_5H_4 \cdot N(CH_3)_2 \cdot C_7H_5(NH_5) \cdot NH$, results from ordinary toluylene diamine

(p. 95) by oxidizing it mixed with dimethyl-p-phenylenediamine, or by the action of IICI-nitroso-dimethylaniline. Its salts with one equivalent of acid are of a beautiful blue color, and are decolorized by an excess of mineral acids with formation of the diacid salts. It is converted into toluylene red (see this) on boiling with water.

The genetic connection of the indamines with the indoanilines and indophenol is shown

in the possibility of converting the simplest indamine into quinone aniline imide, and the latter into quinone-phenol-imide (Möhlau, B. 16, 2843; 18, 2915).

Representatives of the indophenols, indoanilines, and indamines, containing the naphthaline residue are also known in great numbers, and many, like Naphthol Blue (see this) or "Indophenol," have been applied technically (B. 18, 2916).

9. PHENYL-PARAFFIN ALCOHOLS AND THEIR OXIDATION PRODUCTS.

In the preceding sections those classes of aromatic hydrocarbons containing one nucleus were described, which resulted from the substitution of the hydrogen atoms of benzene or the benzene residue of the alkylbenzenes by atoms of other elements or by atomic groups: the halogen substitution products (pp. 57-63), the nitrogen-containing derivatives of the benzene hydrocarbons (p. 63), the aromatic phosphorus, arsenic, antimony, bismuth, boron, silicon, and tin derivatives (pp. 131-133), the phenyl metal compounds (p. 133), the sulpho-acids and their relatives (pp. 133-140), the phenols (p. 140), and the quinones.

Attached to these are those classes of bodies formed by the replacement of hydrogen atoms in the side-groups of the alkylbenzenes. As in the aliphatic series, the oxygen-containing products are considered the most important. Each class of these derivatives is followed by the corresponding halogen, sulphur, and nitrogen compounds, in which all, or at least a part, of the carbon valences, saturated in the principal compounds by oxygen, are taken up with the elements just named. Prominent among these, as with the aliphatic derivatives, are those bodies in

which one carbon atom of an alkyl side-chain is combined with oxygen:

(1a) The monohydric phenyl-paraffin alcohols and their oxidation

products: aldehydes, ketones, carboxylic acids.

Naturally these compounds, as far as the reactivity of the aliphatic residue is concerned, manifest great similarity to the monohydric aliphatic alcohols and their oxidation products (1, 109). This is recalled by their nomenclature and the view that they are phenylsubstitution prod-

ucts of aliphatic substances (p. 32).

Each of these alkyl-benzene derivatives constitutes a starting-out substance from which, by the replacement of hydrogen atoms of the phenyl residue, as with benzene itself, numerous derivatives can be deduced. In general the benzene substitution products of the phenyl fatty bodies, so far as they are worth mention, will be introduced after the corresponding principal bodies. Only the derivatives of monohydric aromatic alcohols, having hydroxyl in their benzene residue, and their oxidation products, which manifest at the same time a phenol character, will be grouped together as—

(1b) Monohydric oxyphenyl-paraffin alcohols and their oxidation prod-

ucts.

Then will follow (2) polyhydric phenyl-paraffin alcohols, in which but one hydroxyl group is joined to a side-chain, and their oxidation products. The conclusion of this section will be (3) polyhydric phenyl-paraffin alcohols, in which more than one hydroxyl group is attached to a side-chain, and their oxidation products.

(11) MONOHYDRIC PHENYL-PARAFFIN ALCOHOLS AND THEIR OXIDATION PRODUCTS.

1. MONOHYDRIC PHENYL-PARAFFIN ALCOHOLS.

The true alcohols of the benzene series are produced by the entrance of an hydroxyl group into the side-chain of an alkylbenzene: primary, secondary, and tertiary. The primary alcohols, upon oxidation, yield aldehydes and acids, the secondary change to ketones:

Formations.—The similarity of benzyl alcohol and its homologues to ethyl alcohol finds expression at the very outset in the methods of producing both classes: (I) by saponification of alkyl benzenes containing an halogen atom in the side-chain—the haloid acid esters of the benzyl alcohols—e. g., benzyl chloride with water alone (A. 196, 353), with water and lead oxide (A. 143, 81), or with potashes. Benzyl alcohols are also produced by converting the chlorides into acetates and saponifying the latter.

(2) By the action of nitrous acid upon primary amines, the reduction products of aro-

matic acid nitriles—e. g., cumo- and hemimellibenzyl alcohol.

(3) By the action of nascent hydrogen on the corresponding aldehydes and ketones.

(4) By heating the aldehydes, or letting them stand with alcoholic or aqueous potash (B. 14, 2394), whereby acids are formed at the same time:

$$2C_6H_6$$
. CHO + KOH = C_6H_6 . CH₂. OH + C_6H_6 . CO₂K.

This reaction we do not observe with the monohydric paraffin alcohols.

(5) By reducing amides of aromatic carboxylic acids, containing the carboxyl group attached to the benzene nucleus, with sodium amalgam in acid solution (B. 24, 173).

(6) By the reduction of unsaturated alcohols: cinnamyl alcohol, $C_aH_aCH = CH_2OH$, becomes hydrocinnamyl alcohol, C_6H_6 . CH_2 . CH_2 . CH_2 . CH_2 . CH_3 .

I, 130).

(7) They are formed in the nucleus-synthetic way when zinc methide acts upon acid chlorides: phenylacetyl chloride and zinc methide yield bensyl dimethyl carbinol (I, 114).;

Benzyl Alcohol, Phenyl Carbinol, [Phenmethylol], C.H.CH.OH, boiling at 206°, with sp. gravity 1.062 (0°), is isomeric with the cresols (p. 144). It occurs as benzyl-benzoic ester and benzyl-cinnamic ester in the balsams of Peru and Tolu, and in storax (A. 169, 289). It is produced by the methods (1), (2), (3), (4), given above, from benzaldehyde, benzyl chloride, and benzamide. Reactions (1) and (3) are used as methods of preparation. It is a colorless liquid, with a faint aromatic odor. It dissolves with difficulty in water, but readily in alcohol and ether. It yields benzaldehyde and benzoic acid when oxidized. Heated with hydrochloric acid or hydrobromic acid, the OH-group is replaced by halogens. Benzoic acid and toluene result on distilling it with concentrated potash.

History.—As early as 1832 Liebig and Wöhler, in the course of their celebrated investigation upon the radical benzoyl, had this alcohol in hand as the result of the interaction of alcoholic potash and benzaldehyde (A. 3, 254, 261). Cannizzaro (1853) was the first to discover the alcohol in studying this reaction.

Homologous Benzyl Alcohols.—The primary alcohols are chiefly made by methods (x), (2), (3), (4); hydrocinnamyl alcohol by method (6); the secondary alcohols by method (1), or by the reduction of the ketones according to method (3), and the tertiary alcohols, like benzyldimethyl carbinol, by method (7).

Nucleus Homologous Benzyl Alcohols:

```
M.P. B.P.
34° 223°
liquid 217°
       (B. 24, 174).
                                                                                                                                                                                                             (B. 18, R.66).
                                                                                                                                                                             59° 217°
                                                                                                                                                                                                             (A. 124, 255).
     2.4 Dimethyl Benzyl Al-
                                                                                                                                                                       22° 232° (B. 21, 3085).
liquid 220° (B. 16, 1577).
cohol, . . . . . (CH_3)_1[2,4]C_0H_1[1]CH_1 OH
3.5-Mesityl Alcohol, . . (CH_3)_1[3,5]C_0H_1[1]CH_2 OH
2.4.5-Cumobenzyl Alcohol, (CH_3)_1[2,4,5]C_0H_1[1]CH_2 OH
                      cohol,
                                                                                                                                                                          168°
                                                                                                                                                                                                          (B. 24, 2411).
3,4,5-Hemimellibenzyl Al-
                                                                                                                                                                             78°
          cohol, . . . . . (CH<sub>3</sub>)<sub>3</sub>[3,4,5]C<sub>6</sub>H<sub>2</sub>[1]CH<sub>2</sub>.OH
Mellithyl Alcohol, . (CH<sub>3</sub>)<sub>5</sub>C<sub>6</sub>.CH<sub>2</sub>OH
p-Cumin Alcohol, . . (CH<sub>3</sub>)<sub>2</sub>CH[4]C<sub>6</sub>H<sub>4</sub>[1]CH<sub>2</sub>.OH
                                                                                                                                                                          160°
                                                                                                                                                                                                             (B. 22, 1217).
Other homologues are the phenyl ethyl alcohols:

Benzyl Carbinol, C<sub>6</sub>H<sub>6</sub>CH<sub>2</sub> CH<sub>2</sub>OH, boils at 212° (B. 9, 373).

Phenyl Methyl Carbinol, C<sub>6</sub>H<sub>8</sub>. CH(OH)CH<sub>2</sub>, boils at 203° (B. 7, 141).

Phenyl Propyl Alcohols: Hydrocinnamyl Alcohol, C<sub>6</sub>H<sub>6</sub>. CH<sub>2</sub>. CH<sub>2</sub>. CH<sub>3</sub>OH, boils at 235°. It is obtained from its cinnamic acid ester, which is present in storax (A. 188,
202). Benzyl Methyl Carbinol, C<sub>6</sub>H<sub>5</sub>. CH<sub>2</sub>. CH(OII). CH<sub>3</sub>, boils at 215°. Phenylethyl Carbinol, C<sub>6</sub>H<sub>5</sub>. CH<sub>2</sub>. CH<sub>3</sub>, boils at 221°. Benzyldimethyl Carbinol, C<sub>6</sub>H<sub>5</sub>. CH<sub>2</sub>. C(OH)(CH<sub>3</sub>)<sub>2</sub>, melts at 21° and boils at 225°.
```

Derivatives of the Phenyl-Paraffin Alcohols.—Haloid Esters. Benzyl chloride and benzyl bromide are produced when chlorine or bromine (p. 61) acts upon boiling toluene (Beilstein, A. 143, 369). Benzyl chloride, bromide, and iodide are also formed from benzyl alcohol and the haloid acids, and benzyl iodide by the action of potassium iodide upon benzyl chloride (A. 224, 126):

```
Benzyl Chloride, . . . C<sub>6</sub>H<sub>6</sub> . CH<sub>2</sub>Cl liquid B. P. 176°.

Benzyl Bromide, . . . C<sub>6</sub>H<sub>6</sub> . CH<sub>2</sub>Br " 210°.

Benzyl Iodide, . . . C<sub>6</sub>H<sub>6</sub> . CH<sub>2</sub>I melts at 24° and decomposes.
```

Benzyl Chloride, isomeric with the three chlortoluenes (p. 61), is an important reagent, by means of which numerous derivatives of benzyl alcohol have been prepared, as its chlorine atom is readily exchanged. It passes into benzyl alcohol when boiled with water. Heated with water and lead nitrate it yields benzaldehyde, and by oxidation benzoic acid:

$$C_6H_6CH_5 \longrightarrow C_6H_5 \cdot CH_1CI - \left\{ \begin{array}{c} \longrightarrow C_6H_5 \cdot CH_1OH \\ \longrightarrow C_6H_5 \cdot CHO \longrightarrow C_6H_5COOH. \end{array} \right.$$

The following ethers have been made by the action of sodium alcoholates upon benzyl chloride: Benzyl Methyl Ether boils at 168°. The ethyl ether boils at 185°. The benzyl ether (A. 241, 374), (C₆H₆CH₂)₂O, boiling at 296°, results from the action of boron trioxide upon benzyl alcohol. Methylene Dibenzyl Ether, CH₂(OCH₂. C₆H₆)₂ (A. 240, 200). Benzylarabinoside, C₅H₉O₅. CH₂. C₆H₅, melts at 172° (B. 27, 2482). Benzylarabinoside and boils at 287°.

Homologous Benzyl Chlorides. a Chlorethyl Benzene, C₂H₅CHCl. CH₃, boils at 194°. (ω) β-Chlorethyl Benzene, C₂H₅. CH₂. CH₂Cl, boils at 93° (17 mm.). o-, m-, p-Methyl Benzyl Chloride, CH₃. C₄H₄CH₂Cl, boil at 198°, 195°, and 192° respectively. a-Chlorpropyl Benzene, C₄H₅. CHCl. CH₂. CH₃, and β-Chlorpropyl Benzene, C₆H₆.

CH₂CHClCH₂, boil about 203-207° with the splitting off of hydrochloric acid and the production of a-phenylpropylene, CaHa. CH: CH. CHa, and allyl benzene, CaHaCHa-

CH = CH₁.
Benzyl Phosphates: The mono- melts at 78°, the di- is liquid, and the tri- melts at 64°

(A. 262, 211).

Esters of Carbonic Acid. Benzyl Acetate, C₆H₅CH₂.O.CO.CH₂, boils at 106°. Dibenzyl Oxalate, (C₆H₅.CH₂O.CO)₂, melts at 80°. Sulphur Derivatives of Benzyl Alcohol are formed just like the sulphur compounds of

the fat-alcohols (I, I47).

Benzyl Sulphydrate, Benzyl Mercaptan, C₆H₅. CH₂. SH. It is a liquid with a leek-like odor; boils at 194°, and at 20° has a specific gravity == 1.058 (A. 140, 86). Benzyl Sulphide, (C₆H₅. CH₂)₂S, melting at 49°, when subjected to dry distillation yields stilbene (see this), stilbene sulphide, dibenzyl (see this), thionessal or tetraphenylthiophiene (see this), and toluene. The sulphone, (C₆H₅. CH₂)₂SO₂, melts at 150°. It results when the sulphoxide in glacial acetic acid is acted upon by KMnO₄ (B. 13, 1284).

Bensyl Disulphide, (C6H5CH2)2S2, melting at 71° (B. 20, 15), results from the oxida-

tion of benzyl sulphydrate in the air (A. 136, 86).

Benzyl Dimethyl Sulphine lodide, CaHaCHaS(CHa), I, is an orange-red colored compound (B. 7, 1274).

compound (B. 7, 1274).

Benzyl Sulphoxide, (C₆H₆CH₂)₂SO, melting at 133°, is formed by oxidizing benzyl sulphide with nitric acid (B. 13, 1284).

Benzyl Sulphonic Acid, C₆H₅. CH₂. SO₃H, is a deliquescent crystalline mass; it is isomeric with toluene-sulphonic acid. The potassium salt is formed on boiling benzyl chloride with potassium sulphite. The chloride melts at 92° (B. 13, 1287).

Benzyl Hyposulphurous Acid, C₆H₅CH₂SSO₂H, melts at 74° (B. 23, R. 284).

Nitrogen Derivatives of the Phenyl-Paraffin Alcohols.

Phanyl Nitrogen paraffing: When the homologous benzenes are heated in sealed

Phenyl Nitro-paraffins: When the homologous benzenes are heated in sealed tubes with dilute nitric acid the nitro-groups usually enter the side-chains with the formation of phenylnitroparaffins (see I, 154; Konowaloff, B. 28, 1850, R. 235; 29, 2199). By this treatment toluene yields *Phenylnitromethane*, C₆H₅. CH₂. NO₂. This body has also been prepared from nitrobenzalphthalide, as well as from benzyl haloids, but best from the iodide (B. 29, 700) by the action of silver nitrite. It is an oil boiling with decomposition at 226°. It dissolves, like the nitro-paraffins, in sodium hydroxide, forming a sodium salt, from which the oily phenylnitromethane is again regained by the action of CO, or acetic acid. If, however, the sodium salt be precipitated with mineral acids, a crystalline substance, melting at 84°, is obtained. This is isomeric with the oily body and is distinguished from it by the red coloration it yields with ferric chloride, as well as by its electric conductivity. It quickly changes both in solution and when in a free state into the oily isomeride. Its constitution certainly corresponds to the formula adopted for the sodium salts of the nitro-paraffins (1, 155), from which, however, the corresponding free bodies in the fatty series have not been successfully isolated (Hantzsch and O. W. Schultze, B. 29, 2251):

$$C_6H_5$$
. $\overrightarrow{CH_2N()_2} \longrightarrow C_6H_5CH \longrightarrow NONa \longrightarrow C_6H_5$. $\overrightarrow{CH-NOH}$

Neutral Oil

Melts at 84°; acid.

Similar stable and unstable isomerides have also been obtained from the nucleus homologues and substituted phenyl nitro-paraffins.

Phenyl-Paraffin Amines, Benzylamines.—(1) Alcoholic ammonia converts benzyl chloride into mono-, di-, and tri-benzylamines (B. 23, 2971):

C₆H₅CH₂NH₂, (C₆H₅CH₂)₂NH, (C₆H₅CH₂)₃N, Benzylamine, boils at 187°. " " 300°. melts " 91°. Dibenzylamine, Tribenzylamine,

Most of the other methods of producing benzylamine are reactions,

which have been fully discussed in connection with the primary alkylamines.

Benzylamine is formed (2) by the reduction of phenylnitromethane, benzaldoxime, and benzylidene phenylhydrazone (B. 19, 1928, 3232); (3) and (4) by heating benzaldehyde with ammonium formate or formamide (B. 19, 2128; 20, 104), together with di- and tribenzylamine; (5) by the reduction of benzonitrile (B. 20, 1709) and (6) of benzothiamide (B. 21, 51); (7) by saponifying benzylisocyanide or benzyl carbonimide, C₆H₅CH₂NCO (B. 5, 692), and (8) benzyl acetamide, C₆H₅CH₂NHCOCH₃ (B. 12, 1297); (9) by the distillation of phenylamidoacetic acid, C₈H₂CH(NH₂)CO₂H (B. 14, 1969); and (10) by the action of caustic alkali and bromine upon a-toluamide. Benzylamine is a liquid, dissolving readily in water. It differs from its isomeric toluidine in being a strong base, which attracts CO₂ from the air.

Homologous Benzylamines are isomeric with corresponding alphylamines (p. 164). They are mostly formed by reducing nitriles with alcohol and sodium; some by the reduction of oximes or nitro-compounds, while others are obtained by the methods indicated under benzylamine.

```
B. P.
197° (B. 26, 1904).
187° (B. 27, 2306).
201° (B. 23, 1026).

      β-Phenylethylamine,
      C<sub>4</sub>H<sub>5</sub>. CH<sub>2</sub>. CH<sub>2</sub>NH<sub>4</sub>
      197° (B. 26, 1904).

      α-Phenylethylamine,
      C<sub>4</sub>H<sub>5</sub>. CH(NH<sub>2</sub>). CH<sub>3</sub>.
      187° (B. 27, 2306).

      ο-Tolubenzylamine,
      CH<sub>3</sub>[2]C<sub>6</sub>H<sub>4</sub>[1]CH<sub>2</sub>NH<sub>2</sub>.
      201° (B. 23, 1026).

      m-Xylylamine,
      CH<sub>3</sub>[3]C<sub>4</sub>H<sub>4</sub>[1]CH<sub>2</sub>NH<sub>2</sub>.
      201° (B. 23, 3165).

      [1'-Amino-1,4-dimethylphene],
      CH<sub>3</sub>[4]C<sub>4</sub>H<sub>2</sub> CH<sub>2</sub>. NH<sub>3</sub>.
      221° (B. 27, 2309).

      β-Phenyl-propylamine,
      CH<sub>3</sub> CH<sub>2</sub> CH<sub>2</sub>. CH<sub>3</sub>. NH<sub>3</sub>.
      210° (B. 26, 2875).

      β-Phenyl-propylamine,
      CH<sub>3</sub> CH<sub>2</sub> CH<sub>3</sub>. CH<sub>3</sub>. NH<sub>3</sub>.
      205°.

      β-Phenyl-isopropylamine,
      CH<sub>3</sub> CH<sub>2</sub>. CH<sub>3</sub> CH<sub>3</sub>[1]CH<sub>3</sub>. NH<sub>3</sub>.
      203° (B. 20, 618).

      [1'-Amino-1,2,4-trimethylphene], (CH<sub>3</sub>)<sub>2</sub>[2,4]C<sub>4</sub>H<sub>3</sub>[1]CH<sub>2</sub>. NH<sub>3</sub>.
      218° (B. 21, 3083).

      ω-Mesitylamine,
      (CH<sub>3</sub>)<sub>2</sub>[3,5]C<sub>4</sub>H<sub>3</sub>[1]CH<sub>2</sub>. NH<sub>3</sub>.
      218° (B. 25, 3013).

      Cumylamine,
      (CH<sub>3</sub>)<sub>2</sub>CH[4]C<sub>4</sub>H<sub>4</sub>[1]CH<sub>2</sub>NH<sub>4</sub>.
      226° (B. 20, 2414).

                                        Cumobenzylamine, . . . (CH_3)_3[2,4,5]C_6H_2[1]CH_2NH_3, 64^{\circ} (B. 24, 2409). Hemimellibenzylamine, . . (CH_3)_3[3,4,5]C_6H_2[1]CH_2NH_3, 123^{\circ} (B. 24, 2411).
```

An optically active, lævorotatory base (B. 29, 2313) has been isolated by means of its bitartrate from a-phenylethylamine, CaHaCH(NHa)CHa, containing an asymmetric C-atom.

Benzylalkyl- and benzylalphylamines, as well as benzylalkylammonium compounds,

attach themselves to the true benzylamines.

Benzylaniline, CeHs. CH2. NH. CeH5, melts at 32°, and is formed from aniline and benzyl chloride (A. 138, 225), or by the reduction of benzylidene aniline with sodium in alcoholic solution (A. 241, 330). When heated to 220° with sulphur it yields thiobenz-anilide, and benzenylamidothiophenol at 250° (A. 259, 300).

Dibenzylamiline, (C₄H₅. CH₂)₂. N. C₆H₅, melts at 67° (B. 20, 1611).

Benzyl Chloramine (B. 26, R. 188). Dibenzyl Nitrosamine, (C₄H₆CH₂)₂N. NO,

melts at 61° (B. 19, 3288). Benzyl Methyl Nitramine, CaHaCHaN(CHa)NO. (B. 29,

Benzyl Oxethylamine, C₆H₆.CH₂.NH.CH₂.CH₂OH, pierate, melting at 136°, results from the rupture of the phenyloxazoline ring, C₆H₆.C O-CH₂ (see this), by sodium and alcohol (B. 29, 2382).

The following representatives of the numerous benzylated acid amides and benzylated

nitrogen derivatives of carbonic acid may be mentioned:

Benzylacetamide, C₆H₆CH₂NHCOCH₅, melts at 60° (B. 19, 1286).

Dibenzyl Urea Chloride, (C₆H₆CH₂)NCOCl, is an oil (B. 25, 1819).

Benzyl Urea, C₈H₆CH₂NHCONH₂, melts at 147°. Sym. and unsym. cibenzyl

area melt at 107° and 124° (B. 9, 81).

Tri- and letra-benzyl urea melt at 119° and 85° (B. 25, 1826).

Benzylthiourea melts at 164° (B. 24, 2727; 25, 817).

Bibenzyl Guanidine, (C₆H₅CH₂NH)₃C: NH, melts at 100° (B. 5, 695).

Benzylisocyanate, Benzyl carbonimide, C₆H₅CH₂N: CO, is a liquid with penetrating odor.

Benzylcyanurate melts at 157° (B. 5, 692).

Benzyl Mustard Oil, C₆H₆CH₇N: CS, boils at 243° (B. 1, 201).

Dibenzylhydrazine, C₆H₅, CH₂. NH. NH. CH₃.

C₆H₅, melting at 65°, is formed when benzalazine (D. 185) is reduced. It yields (CH,N)₁, we evidentical scide recover the latter into benzalezine and dibenzylhydra. on oxidation. Concentrated acids resolve the latter into benzalazine and dibenzylhydrazine (B. 28, 2345).

Benzylhydroxylamines.—Liquid a-benzylhydroxylamine, CaHaCH2O. NH2, boiling at 123° (50 mm.), results upon decomposing benzyl benzaldoxime with hydrochloric acid.

Benzyl chloride changes this liquid substance to

aβ-Dibenzylhydroxylamine, C₆H₅CH₂.O.NH.CH₂.C₆H₅, liquid, and Tribenzylhydroxylamine, C.H.CH. O. N(CH. C.H.).

 β -Benzylhydroxylamine is obtained by decomposing $a\beta$ -dibenzylhydroxylamine with hydrochloric acid. It melts at 57°. Benzyl chloride converts it into β dibenzylhydroxylamine, (CoH5CH2)2N. OH, melting at 123° (A. 275, 133); compare also the bentaldoximes, p. 185.

β-Bis-o-nitrobenzylhydroxylamine, (NO₂. C₈H₄. CH₂), N. OH, melting at 24°, is obtained from o-nitrobenzyl chloride and hydroxylamine. Nitrobenzylisonitrobenzaldox-

ime is formed by its oxidation (p. 187) (B. 30, 58).

Substituted benzyl alcohols are derived from substituted benzyl chlorides when they are heated with aqueous potash (B. 25, 3290), or by means of acetic esters. Many, like m nitrobenzyl alcohol, are also obtained by the action of alcoholic potash upon the corresponding aldehydes.

- o-, m-, p-Brombenzyl Alcohol: o- melts at 80°; m- is liquid; p- melts at 72°.
- o-, m-, p-Brombenzyl Bromide, melt at 30°, 41°, 61°.
 o-, m-, p-Nitrobenzyl Alcohol, "74°, 27°, 93°.
 o-, m-, p-Nitrobenzyl Chloride, "47°, 46°, 71°.

Formation of Hetero-rings from Derivatives of o-Amidobensyl Alcohol.—Just like the o-diamines (p. 95), o-amidophenols (p. 152), and o-amidothiophenols (p. 157), many o amidobenzyl alcohol derivatives, and also those of o-nitrobenzyl alcohol, so far as they yield o amidobenzyl alcohol compounds upon reduction, show ability to form heterorings. Some of the derivatives of these two alcohols capable of yielding hetero-rings

o-Nitrobenzyl Sulphocyanide, NO₄C₆H₄CH₂S. CN, melting at 75° (B. 25, 3028), yields o-benzylene-\$\psi\$-thiourea. Sulphuric acid reduces it to o-nitrobenzylcarbamine-thiolic ester, NO₂. C₆H₄CH₂. SCONH₄, melting at 116°. Hydrochloric acid saponifies this to o-nitrobenzyl mercaptan, NO₂[2]C₆H₄[1]CH₂SH, melting at 43°. Both bodies yield benzisothiazole upon reduction (B. 28, 1027; 29, 160).

o Amidobenzyl Alcohol, Calla(NH2). CH2. OH, melting at 82° and boiling at 160°, is formed by the reduction of anthranil and o-nitrobenzyl alcohol with zinc-dust and hydrochloric acid (B. 25, 2968; 27, 3513). It becomes thiocumazone (B. 27, 1866) when it is boiled with alcoholic CS₂, and thiocumothiazone (B. 27, 2427) when the CS₂ and alcoholic potash are used. The urea derivatives of o-amidobenzyl alcohol lead to similar rings (B. 27, 2413)

o. Amidobenzyl Chloride Hydrochloride, HCl. NH, . C. H. CH, Cl, is formed by the action of concentrated hydrochloric acid upon o-amidobenzyl alcohol. With caustic potash this salt yields poly-o-benzylene-imide, (C₇H₇N)x (B. 19, 1611; 28, 918, 1651); with acetic anhydride, μ -methylphenpentoxazole, with thiacetamide μ -methylphenpenthiazole (B. 27, 3515), and with thiurea, o-benzylene-ψ-thiurea (B. 28, 1039); compare

o-nitrobenzylrhodanide.

An anhydride of an o-bensylalcohol sulphonic acid, $C_6H_4\left\{\begin{bmatrix} I\\2\end{bmatrix}CH_2SO_5\right\}$, melting with decomposition at 288°, has been obtained by reduction of o-sulphobenzoic chloride, just as phthalide has been formed from phthalyl chloride (B. 27, R. 790).

$$\begin{array}{c} C_{6}H_{4} \left\{ \begin{matrix} CH_{3}.SCN & H \\ NO_{3} \end{matrix} \right\} \\ C_{6}H_{4} \left\{ \begin{matrix} CH_{3}CI \\ NH_{3}HCI \end{matrix} + \frac{Thiocarbamide}{Thiocarbamide} \right\} \\ C_{6}H_{4} \left\{ \begin{matrix} CH_{3}-S \\ NH - C \end{matrix} : \begin{matrix} NH & \text{or } C_{6}H_{4} \\ NH - C \end{matrix} : \begin{matrix} CH_{3}-S \\ NH - C \end{matrix} + \frac{C}{NH_{2}} \\ NH - C \end{matrix} \right\} \\ C_{6}H_{4} \left\{ \begin{matrix} CH_{3}.SH & 2H & C_{6}H_{4} \\ NO_{3} \end{matrix} \right\} \\ C_{6}H_{4} \left\{ \begin{matrix} CH_{3}.SH & 2H & C_{6}H_{4} \\ NH - C \end{matrix} \right\} \\ C_{6}H_{4} \left\{ \begin{matrix} CH_{3}-O \\ NH - C \end{matrix} \right\} \\ C_{6}H_{4} \left\{ \begin{matrix} CH_{3}-O \\ NH - C \end{matrix} \right\} \\ CH_{3}-S & Thiocumazone \end{matrix} \\ C_{6}H_{4} \left\{ \begin{matrix} CH_{3}CI \\ NH_{3}+C \end{matrix} \right\} \\ C_{6}H_{4} \left\{ \begin{matrix} CH_{3}-C \\ NH_{3}-C \end{matrix} \right\} \\ CH_{3}-C \end{matrix} \\ C_{6}H_{4} \left\{ \begin{matrix} CH_{3}-C \\ NH_{3}+C \end{matrix} \right\} \\ CH_{3}-C \end{matrix} \\ C_{6}H_{4} \left\{ \begin{matrix} CH_{3}-C \\ NH_{3}+C \end{matrix} \right\} \\ CH_{3}-C \end{matrix} \\ CH_{3}-C \end{matrix} \\ CH_{3}-C \end{matrix} \\ CH_{3}-C \end{matrix} \\ CH_{4}-C \end{matrix} \\ CH_{5}-C \end{matrix} \\ CH_{$$

o-Nitrobenzylamine, $C_6H_4(NO_2)$. CH_2 . NH_2 , obtained from o-nitrobenzylchloride by the saponification of its phthalimide-derivative, is a strong, oily base (B. 20, 2227). o-Nitrobenzylformamide, NO_2 . C_6H_4 . CH_2 . NH. CHO, melting at 89°, is reduced to dihydroquinazoline (see this) (B. 25, 3031). p-Nitrobenzylamine—see B. 30, 61. o-Nitrobenzyl Aniline, NO_2 . C_6H_4 . CH_2 . NHC_6H_5 , melts at 44° (B. 19, 1607). o-Nitrobenzylphenylnitrosamine, $NO_2C_6H_4CH_2N(NO)C_6H_5$, is converted by tin and hydrochloric acid into n-phenylindazole (B. 27, 2899). o-Amidobenzylamine, o-benzylenediamine, $NH_2C_6H_4CH_2NH_2$, is a radiating crystallor mass, obtained from o-nitrobenzylamine. With aldehydes like benzaldchyde it forms thenylletrahydroketoguinazoline: with phosgene, letrahydroketoguinazoline: with

forms phenyltetrahydroketoquinazoline; with phosgene, tetrahydroketoquinazoline; with carbon disulphide, tetrahydrothioquinazoline (B. 28, R. 238). o-Amidobenzyl Aniline, NH₂. C₆H₄. CH₂. NH. C₆H₅, melting at 86°, forms β-phenphenyldihydrotriazine with nitrous acid (B. 25, 448):

2. AROMATIC MONALDEHYDES.

The aromatic monaldehydes are the first oxidation products, and correspond to the primary aromatic monohydric alcohols. They are very similar to the fatty aldehydes so far as their rearrangements, dependent

upon the reactivity of the aldehyde group, are concerned.

Formation.—(1) By the oxidation of the primary monohydric, aromatic alcohols. (2) By the distillation of the calcium salts of the aromatic acids with calcium formate. (3) From their halogen derivatives, C_6H_1 .—CHCl₂, with water, especially in the presence of sodium carbonate, lime, or lead oxide, or by heating with anhydrous oxalic acid. (4) Technically by oxidizing benzyl chloride with lead nitrate. (5) A very interesting and direct conversion of homologous benzenes into aldehydes is that occurring in the action of chromyl chloride, CrO_1Cl_2 . The first products are pulverulent, brown addition-compounds, $C_6H_6CH_3(CrO_1Cl_2)$, which decompose into aldehydes when they are introduced into water (B. 17, 1462; 21, R. 714).

Properties. — Benzaldehyde and its homologues are mostly liquid bodies, which possess an aromatic odor and reduce ammoniacal silver solutions with the production of a metallic mirror. (1) They are readily oxidized to carboxylic acids. (2) They differ from the fatty aldehydes in that they are, as a general thing, readily oxidized to alcohols and acids by alcoholic or aqueous alkalies (p. 176); it appears that this reaction is, however, only peculiar to those aldehydes in which the CHO-group is in direct union with the benzene nucleus. (3) Nascent hydrogen reduces them to alcohols when they are in part, through the union of two aldehyde residues, converted into hydrobenzoins. (4) They combine with acid (5) With hydroxylamine they yield aldoximes, which alkaline sulphites. manifest rather remarkable isomeric relations. (6) They form phenylhydrazones with phenylhydrazine. (7) Phosphorus pentachloride replaces their aldehyde oxygen by two atoms of chlorine. (8) Chlorine substitutes aldehyde hydrogen.

They do not polymerize, as do the first members of the group of fatty

aldehydes.

Nucleus Syntheses.—(1) In the reduction of aromatic aldehydes—e. g., in the electrolytic reduction (B. 29, R. 229)—there occurs, along with alcohol formation, a production of hydrobenzoin analogous to the pinacone formation (1, 212):

$$2C_6H_5$$
. CHO + $2H = C_6H_5$ CH(OH) — CH(OH). C_6H_5 —Hydrobenzoin.

(2) A very interesting reaction of the aldehydes is their conversion into benzoins through the agency of alcoholic potassium cyanide. Two aldehyde molecules combine to a polymeric body:

$$2C_6II_5CIIO = C_6H_5CII(OH)$$
. CO. C_6H_6 —Benzoin.

See B. 29, 1729, for the condensations of benzylidene aniline and benzaldehyde by potassium cyanide.

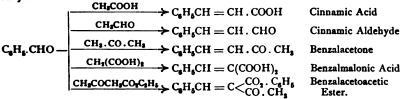
(3) The aromatic aldehydes combine with the most heterogeneous

bodies,—e. g., aldehydes, ketones, monocarboxylic acids, dicarboxylic acids, etc.,—water always disappearing.

These so-called condensation-reactions proceed similarly to the aldol-condensation, only there is generally an elimination of water, as in the conversion of aldol into croton-aldehyde. The condensation agents are HCl-gas, zinc chloride, sulphuric acid, glacial acetic acid, acetic anhydride, dilute sodium hydroxide, baryta-water, a solution of potassium acetate, and potassium cyanide.

In this manner benzaldehyde can undergo the following rearrangements without diffi-

culty:



Pyrones, CO[C(CH₃): C(C₄H₅)]₃O (B. 29, 1352), result when two molecules of benzaldehyde condense with ketones like diethylketone. Pyridine derivatives result when benzaldehyde and acetoacetic ester condense with ammonia and aniline; whereas benzylidene diacetoacetic esters are formed under the influence of aliphatic amines (B. 29, R. 841).

The benzaldehydes also condense with phenols and anilines, forming derivatives of

triphenylmethane.

The conditions under which these bodies are formed will be more fully

explained in connection with their description.

Benzaldehyde, Bitter Almond Oil, Benzyl Hydride, C₆H₅. CHO, boiling at 179°, with sp. gravity 1.050 (15°), is a colorless liquid with high refractive power. Formerly it was prepared exclusively from its glucoside amygdalin (see below). At present it is only the officinal bitter-almond oil water, aqua amygdalarum amararum, in which hydrocyanic acid is the active ingredient, that is made from the amygdalin. It has the characteristic agreeable "bitter-almond oil" odor. It is soluble in 30 parts water, and is miscible with alcohol and ether. Benzaldehyde does not occur already formed in the bitter almonds, but is produced, as demonstrated by Wöhler and Liebig in 1831, from the glucoside amygdalin, contained in the oil. This is easily converted by boiling with dilute acids or upon standing in contact with the unorganized ferment emulsin, also present in bitter almonds, into benzaldehyde, glucose, and hydrocyanic acid. Amygdalin:

$$C_{20}H_{27}NO_{11} + 2H_{2}O = C_{6}H_{6}CHO + 2C_{6}H_{12}O_{6} + CNH.$$

In the general methods common to the formation of all aldehydes reactions were indicated which would lead to the production of benzal-dehyde. Thus it is formed (1) from benzyl alcohol; (2) from calcium benzoate and formate; (3) from benzal chloride; (4) from benzyl chloride, from which it is prepared technically by oxidation with lead nitrate; and (5) from toluene and chromyl chloride, CrO₂Cl₂.

In describing the transformations of the aldehydes, benzaldehyde was

chosen as the example. It even absorbs oxygen from the air and becomes benzoic acid, and when mixed with acetic anhydride and sand it not only yields benzoic acid, but also benzoyl peroxide (C₆H₅COO)₂ (see this) (B. 27, 1959). Sodium amalgam reduces it to benzyl alcohol and hydrobenzoin, while PCls changes it to benzal chloride. It shows both oxime and phenylhydrazone formation, etc.

Homologous Benzaldehydes.—o-, m-, and p-Toluic Aldehydes boil at 200°, 199°, The o- and m-bodies smell like benzaldehyde, while the p-compound has an

odor like that of pepper.

a Toluic Aldehyde, Phenylacetaldehyde, $C_a II_b$. CH₂. CHO, boiling at 206° and isomeric with the three toluic aldehydes, is produced (1) by distillation of a toluate of calcium and calcium formate; (2) when chromyl chloride and water act upon ethyl benzene; (3) by acting with water on β -bromstyrolene; (4) by heating phenyl-lactic acid or phenyl-glycidic acid with dilute sulphuric acid; (5) from phenyl-a-chlor-lactic acid, $C_6 II_5$. CH(OH). CHCl. CO₂H, by the action of alkalies (B. 16, 1286; A. 219, 179); and (6) from phenyl-glyceric acid at 160°.

Phenyl-propyl Aldehyde, hydrocinnamic aldehyde, CaHa. CHa. CHo,

boils at 208°.

Cumic Aldehyde, Cuminol, p-isopropyl-benzaldehyde, (CH₃)₂CH-[4]C₆H₄[1]CHO, boiling at 235°, with specific gravity 0.973 (13°), occurs, together with cymene, in Roman caraway oil, and in oil of Cicula virosa, or water hemlock (B. 26, R. 684). Cuminol possesses an aromatic odor. Dilute nitric acid oxidizes it to cumic acid; chromic acid converts it into terephthalic acid. Cumic acid (see this) and cumyl alcohol (p. 177) are produced when it is digested with alcoholic potash. When distilled with zinc-dust, cymene results.

Derivatives of Benzaldehyde.

Haloid Derivatives.—The halogen compounds corresponding to benzaldehyde are

obtained by the action of PCl₅ or PBr₅ upon it.

Benzal Chloride, Benzylidene Chloride, Chlorobenzene, Chloride of Bitter-almond Oil, C₆II₃CHCl₄, boiling at 213°, with sp. gravity 1.295 (16°), results from the action of chlorine upon boiling toluene, from toluene (A. 139, 318; 146, 322) and PCl₅ at 170-200°, as well as from benzaldehyde and COCl₅ (Z. f. Ch. [2] 7, 79). It changes to benzaldehyde when it is heated to 140-160° with water, or to 60-70° with anhydrous

oxalic acid. Bensal Bromide boils at 130-140° (20 mm.).

Ethers and Esters of Bensaldehyde.—Bensal dimethyl and diethyl ether, boiling at 208° and 222°, bensal diacetyl ester, melting at 44° and boiling at 220° (A. 102, 368; 146, 323), are produced when sodium methylate, sodium ethylate, and silver acetate act upon benzal chloride. The diethyl ether is also formed from benzaldehyde and orthoformic

ester (1, 233; B. 29, 247), as well as from benzylideneimide hydrochloride with alcohol. Sulphur Derivatives of Benzaldehyde.—Compare the thioacetaldehydes (1, 203):aand 3-trithiobenzaldehyde melt at 167° and 225° (B. 29, 159). Polymeric thiobenzaldehyde melt at 167° and 225° (B. 29, 159). Polymeric thiobenzaldehyde melts at 83° (B. 24, 1428). When heated with finely divided copper they yield stilbene, C₆H₅.CH = CH. C₆H₅ (see this). Polassium Oxybenzylsulphonate, C₆H₅CH(OH)SO₃K + ½H₂O (Bertagnini, A. 85, 186).

Benzaldehyde Nitrogen Derivatives.—In its deportment toward ammonia benzaldehyde

approaches formaldehyde more closely than it does acetaldehyde, in that it forms-

Hydrobenzamide, tribenzal-diamine, (C6H5CH), N2, melting at 110°. When this body is heated it is transposed to amarine or triphenyldihydroglyoxaline (see this). When hydrochloric acid gas is conducted into the alcoholic-benzene solution of hydrobenzamide, benzylidene imide, CallaCH: NH. HCl, melting with decomposition at Water immediately resolves this body into benzaldehyde and ammo-180°, separates. nium chloride (B. 29, 2144).

Benzal Ethylamine, C₆H₅. CH: N. C₂H₅, boils at 195°. Benzal Aniline, Benzylidene Aniline, C₆H₅. CH: N. C₆H₅, melts at 45°.

When the o-phenylenediamines and benzaldehyde interact the bodies resulting at first are: Benzylidene-o-phenylenediamine, NH₂. C₆H₄N: CH. C₆H₅, melting at 61°, and dibenzylidene-o-phenylenediamine, C₆H₆[N: CH. C₆H₅]₂. However, they readily rearrange themselves into isomeric, ring-shaped imidazole derivatives or aldehydines (p. 96) (B. **29**, **14**97).

Benzylidene-hydrazine, CaHa. CH: NNH2, melting at 16° and boiling at 140° (14 mm.), and obtained from hydrazine hydrate with benzaldehyde and barium oxide (J. pr. Ch. [2] 44, 539), passes through a number of reactions, splitting off hydrazine,

Bensalezine, C₆H₅CH: N₂: CH. C₆H₆, melting at 93°. When this compound is beated it breaks down into nitrogen and stilbene (see this). It yields dibenzyl hydrazine (p. 180) upon reduction, and combines with bromine to a tetrabromide, which decomposes very readily, with evolution of nitrogen (B. 28, 2345).

Benzal-phenylhydrazone, C₈H₆CH: NNHC₆H₅, melting at 152° (A. 190, 134), becomes dibenzal diphenylhydrotetrazone when it is oxidized (p. 128).

Numerous benzal-compounds of hydrazine derivatives have been prepared; they serve to characterize the latter.

Benzhydrazoin, C₆H₅. CH N. C₆H₅, melting at 55°, is formed from benzalde-hyde and hydrazobenzene (p. 117), at 120°-150° (B. 19, 2239).

Benzaldoximes.—The interaction of hydroxylamine and benzaldehyde produces
a-Benzaldoxime, benzantialdoxime, melting at 35° and boiling at 117° (14 mm.).
Hydrochloric acid, sulphuric acid, or bromine changes it, with the simultaneous producaldoxime, melting at 125°. When this body is distilled under reduced pressure it passes into the a-derivative. Each of these isomerides gives rise to two structurally isomeric series of alkyl ethers, in one of which the alkyl is joined to oxygen, in the other to nitrogen, as the first, upon decomposition, yield α , and the second β -alkyl hydroxylamines. Hantzsch and Werner attribute the isomerism of the a- and β -aldoximes to the spacial arrangement of the hydroxyl group with reference to nitrogen. The oximes are distinguished as benzanti- and benzsynaldoxime (B. 24, 3481). The syn-configuration would fall to the β -aldoxime, because in a series of reactions—e. g., treatment of the acid ester with alkalies—it changes more readily and completely to benzonitrile than the a-body:

(a-) Benzantialdoxime
$$\begin{array}{c} C_0H_5 \cdot CH \\ HON \end{array}$$
 (β -)Benzsynaldoxime $\begin{array}{c} C_0H_5CII \\ \parallel \\ NOIH \end{array}$

The following formulas would then correspond to the N- and O-alkyl ethers of these compounds:

Antialkyl C₆H₆—CH
$$\leftarrow$$
 \leftarrow C₆H₆CHO \leftarrow \rightarrow C₆H₆CHO \leftarrow \rightarrow CH₂ONH₂ \leftarrow \rightarrow CH₂ONH₂ \leftarrow \rightarrow C₆H₆CHO \leftarrow \rightarrow C₆H₆CH \rightarrow C₆H₆CHO \leftarrow \rightarrow C₆H₆CH \rightarrow CH₂ \rightarrow CH₂OH₆CH \rightarrow CH₆CH \rightarrow CH

The benzaldoximes and phenylcyanate combine to isomeric phenylurethane derivatives, C_aH_aCH: NOCONHC_aH_a. The N-alkyl ethers also unite with phenylcyanate, forming azoxazole- (furo-ab'-diazole-) derivatives (B. 27, 1957):

$$C_6H_6$$
. CH C_4H_6 CO C_6H_6 CH CO C_6H_6 CO CO

Antibenzaldoxime-o-methyl Ether is an oil, boiling at 191°. It results from the interaction of a-benzaldoxime with sodium alcoholate and methyl iodide. Hydrochloric acid resolves it into benzaldehyde and a-methylhydroxylamine. N-Methyl Ether melts at 45-49°. Its hydrobromide is formed on heating a benzaldoxime, methyl bromide and methyl alcohol in a sealed tube to 85°. On exposure it rearranges itself into the synform (B. 29, R. 866). Synbenzaldoxime-N-methyl Ether, melting at 82°, is formed, together with the isomeric o-ether (which appears not to have been isolated), from synbenzaldoxime, methyl iodide, and sodium ethylate (B. 24, 2812).

N-Phenylbenzaldoxime, Ce HaCH < NCa Ha, melting at 109°, results from the union of

benzaldehyde with \(\beta\)-phenylhydroxylamine (p. 70) (B. 27, 1958).

Benzantialdoxime Acetate, C.H.CHNO(OC. CH2), melts at 15° (B. 27, R. 599).

Benzaldoxime Ocetic Acid, C.H.CHN(OCH2COOH), melts at 98°, the N-derivative, $C_6H_5CH< N.CH_2.COOH$ at 183° with decomposition. They are formed when

chloracetic acid acts upon potassium benzaldoxime. When decomposed the first yields glycollic acid and the second amidoxylacetic acid, HO. NH. CH., COOH (1, 350) (B. 29, R. 169).

Benzalamido-sulphonic acid, CaHa. CH: NSOaH, results from benzaldehyde and amido-sulphonic acid (B. 25, 472).

Many substituted benzaldoximes, ketoximes, the benzildioximes, etc., show isomerk

relations similar to those exhibited by the benzaldoximes. Substituted Benzaldehydes deport themselves toward oxidizing and condensing agents the same as benzaldehyde itself. The formation of heterocyclic bodies from o-nitro- and o-amidobenzaldehyde is especially worthy of notice.

Haloid Benzaldehydes are formed when oxalic acid or sulphuric acid (A. 272, 148) acts upon the halogen benzal chlorides; or by oxidizing cinnamic acids containing halo gens in the nucleus:

o Chlorbenzaldehyde melts at -4°; boils at 213°; the oxime melts at 75°. 17°; 213°; 70°. m-Chlorbenzaldehyde 213°; p-Chlorbenzaldehyde " 47°; " 106°. 21°; " 37°. o-Iodbensaldehyde .. o-Brombenzaldehyde 73°. 57°; p-Brombenzaldehyde " p-Iodbensaldehyde

See B. 29, 875, for the di- and tetrachlorbensaldehydes.

o., m., p. lodosobenzaldehydes, CaH4(IO)CHO, and o., m., and p. lodobenzaldehydes, 6H4(IO2)(CHO), have been obtained from the corresponding iodide-chlorides (B. 29, R. 774).

Nitrobenzaldehydes, NO₂C₆H₄CHO. On dissolving benzaldehyde in nitric-sulphuric acid, the chief product is meta-nitrobenzaldehyde. o-Nitrobenzaldehyde is formed simultaneously (B. 14, 2803). o-Nitrobenzaldehyde is obtained pure from o-nitrocinnamic acid by oxidizing the alkaline solution with potassium permanganate in the presence of benzene (B. 17, 121), or from o-nitrocinnamic ester through the action of nitric acid and sodium nitrite.

Para-nitrobenzaldehyde results (1) by the oxidation of p-nitrocinnamic acid (B. 14, 2577); (2) by allowing CrO₂Cl₂ and water to act upon p-nitrotoluene in carbon disulphide (li. 19, 1061); (3) when p-nitrobenzyl chloride is boiled with water and lead nitrate, or when sulphuric acid acts upon p-nitrobenzal chloride:

```
M. P. 97° (a), 136° (\beta); hydrasone, 117° (a), 118° (\beta);
                              M.P.
o-Nitrobenzaldehyde, 46°; oxime, m-Nitrobenzaldehyde, 58°; "
                                                    129° (a), 174° (β);
p-Nitrobensaldehyde, 107°;
                                           66
```

Compare B. 25, 2457, for the deportment of the nitrobenzaldehydes in the animal organism. o-Nitrobenzaldehyde condenses with aldehyde and acetone through the action of dilute caustic soda to o-nitrophenyllactic acid aldehyde and o-nitrophenyllactic methyl ketone, which caustic soda converts into indigo:

$$c_{eH_4} \left\{ \begin{bmatrix} \mathbf{I} \end{bmatrix}_{CHO}^{CHO} - \left\{ \begin{array}{c} \frac{CH_8 \cdot CHO}{C_0H_4} \left\{ \begin{array}{c} CH(OH) \cdot CH_2 \cdot CHO \\ NO_2 \end{array} \right\} \right. \\ \left. \frac{(CH_9)_7CO}{NO_2} + C_0H_4 \left\{ \begin{array}{c} CH(OH) \cdot CH_2 \cdot CO \cdot CH_3 \end{array} \right\} \right. \\ \left. \frac{CO}{NH} \left\{ \begin{array}{c} CO \\ NH \end{array} \right\} C_0H_4 \left\{ \begin{array}{c} CO \\ NH \end{array} \right\} C_0$$

When the nitrobenzaldehydes are reduced electrolytically the first products are aldekydophenylkydroxylamines, CHO. C.H. NHOH, which, however, immediately combine with the unaltered nitrobenzaldehyde to N-aldehydophenyl-nitrobenzaldoxime,

NO₂C₈H₄CH N. C₈H₄CHO (p. 185) (B. 29, 3037; 28, 250). Ferric chloride oxidizes

this condensation-product to nitrosobenzaldehyde, NO.
$$C_6H_4$$
. CHO.

N-o-Nitrobenzyl-o-nitrobenzaldoxime, NO₂. C_6H_4 . CH \searrow

N . CH₂. C_6H_4 . NO₂, melti-

ing at 142°, results upon oxidizing bis-o-nitrobenzylhydroxylamine (p. 180) (B. 30, 58). 5-Nitro-2-chlorbenzaldehyde, NO₃. C₆H₃Cl. CHO, melts at 80°; its oxime at 147°. The latter is readily converted by boiling alkali into nitrosalicylic acid (B. 26, 1253). 3-Nitro-4-brombenzaldehyde, NO₂. C₆H₃BrCHO, melts at 103°; its oxime at 145°

Amidobenzaldehydes, NH₂C₈H₄CHO. The o- and p- bodies are obtained in the action of ferric chloride upon their oximes, which are formed by the reduction of o- and p-nitrobenzaldoximes with ammonium sulphide (B. 15, 2004; 16, 1998).

o Amidobenzaldehyde is also obtained by reducing o-nitrobenzaldehyde and anthranil (see this) with ferrous sulphate and ammonia (B. 17, 456). m-Amidobenzaldehyde is formed when m-nitrobenzaldehyde is reduced with tin and glacial acetic acid.

o-Amidobenzaldehyde melts at 39°; its oxime at 132°; its acet-derivative at 70°. m-Amidobenzaldehyde is yellow and amorphous; "88°; ""—. p-Amidobenzaldehyde . . . melts at 70°;

p-Dimethyl- and p-Diethylamidobenzaldehydes, melting at 73° and 81°, are obtained when the condensation-products from chloral and dialkyl aniline-e.g., p-dimethylamidophenyl-trichlorethyl alcohol, (CH₈), NC₈H₄CH(OH)CCl₈—are acted upon with alcoholic potash (B. 19, 365). p-Dimethylamidobenzaldehyde condenses to hexamethylleucaniline (see triphenylmethane dyes) with dimethylaniline.

The Hetero-ring Formations of o-Amidobenzaldehyde.—o-Amidobenzaldehyde combines especially readily with compounds containing a CH₂-CO group, in the presence of dilute caustic soda. The products resulting at first are of an aldol nature, for they immediately split off water and yield quinoline or its derivatives. o-Amidobenzaldehyde combines with acetaldehyde to quinoline, with acetone to quinaldine, with malonic acid to \$\beta\$-carbostyril carboxylic acid (B. 25, 1752), and with urea to quinasolon (B. 28, 1037). Alcoholic ammonia transposes the acidyl o amidobenzaldehydes into quinazolines or benzmetadiazines (B. 27, 280, 443):

$$C_{6}H_{4}\left\{\begin{bmatrix}\mathbf{1}\\\mathbf{I}\end{bmatrix}CHO\\\mathbf{C}_{6}H_{4}\right\}\begin{bmatrix}CH=CH\\\mathbf{N}=CH\\\mathbf{C}\end{bmatrix}CH_{2}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\right\}\begin{bmatrix}CH=CH\\\mathbf{N}=C\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}=C\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}=C\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}=C\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}+CO\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}+CO\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}+CO\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}+CO\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}+CO\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}+CO\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}+CO\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}+CO\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}+CO\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}+CO\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{C}\end{bmatrix}CH_{3}\\\mathbf{C}_{6}H_{4}\left\{\begin{bmatrix}\mathbf{C}H_{2}CO_{2}H_{12}\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO\\\mathbf{N}+CO$$

Benzaldehyde-m-Sulphonic Acid, SO₈H. C₉H₄. CHO, white, deliquescent crystals (B. 24, 791).

3. AROMATIC MONO-KETONES.

The oxidation products of the secondary phenyl-paraffin alcohols are mixed ketones, in which an aromatic and an aliphatic hydrocarbon residue are joined by the CO-group. The ketones containing two benzene residues linked by carbonyl, such as benzophenone or diphenyl-ketone, will be discussed later in connection with the corresponding hydrocarbons, like diphenylmethane.

Formation.—Mixed aromatic-aliphatic ketones are usually produced by reactions similar to those employed with the aliphatic ketones

(1) By the oxidation of secondary alcohols, like phenylmethyl carbinol.

(2) When sulphuric acid acts upon phenyl acetylene:

$$C_aH_aC : CH \longrightarrow C_aH_aCOCH_a$$

Nucleus-synthesis: (3) By the distillation of a mixture of calcium salts of an aromatic and a fatty acid. (4) By the action of zinc alkyls on acid chlorides (A. 118, 20). (5) From benzenes by action of fatty acid chlorides and aluminium chloride, carbon disulphide being used as a diluent.

(6) By decomposing β-ketone carboxylic acids—e. g., mono- and dialkyl benzoylacetic acids (B. 16, 2131)—with alcoholic potash.

(7) Acidylated benzenes finally result as a consequence of intramolecular rearrangement upon heating the alkyl ethers of phenylolefine alcohols, which are prepared by the distillation of ortho-ethers of acetophenone. In this way the acidyl benzenes can be built up from acetophenone (Claisen, B. 29, 2931):

$$C_6H_5CO \cdot CH_3 \rightarrow C_6H_5C(OCH_3)_2 \cdot CH_3 \rightarrow C_6H_6C(OCH_3) : CH_3 \rightarrow C_6H_5COCH_2 \cdot CH_3$$

Properties and Deportment.—The mixed aromatic-aliphatic ketones are colorless liquids, insoluble in water, and possess an odor which is not disagreeable.

- (1) Nascent hydrogen converts them into secondary alcohols.
- (2) Chromic acid transforms the ketones C₆H₅. COR into benzoic acid and the alkyl, which is further oxidized.

(3) Potassium permanganate converts them into a-ketonic acids (B. 23, R. 640; 24,

3543; 26, R. 191).

(4) Acids and acid amides, strangely enough, are formed when phenylmethyl ketones are heated with yellow ammonium sulphide:

(5) On heating benzene ketones with sulphuric acid the acetyl-group splits off and benzene sulphonic acids result (B. 19, 2623).

(6) Those ketones in which the CO group is attached to the benzene nucleus do nat.

unite with alkaline bisulphites.

(7) The phenyl-alkyl ketones apparently form but one acetoxime with hydroxylamine; the opposite is true of benzaldehyde.

(8) They form hydrazones with phenylhydrazine.

Acetophenone, Phenylmethyl Ketone, Acetyl Benzene, C.H. CO .-CH₃, melting at 20° and boiling at 202°, crystallizes in large plates. is applied as a hypnotic under the name of hypnone. It is formed (1) from phenylmethyl carbinol; (2) from phenylacetylene; (3) by distilling benzoate of calcium with calcium acetate; (4) by the action of zinc methyl upon benzoyl chloride; (5) from benzene, acetyl chloride, and AlCl₂; (6) from benzoyl acetoacetic ester, C₆H₆CO. CH(COCH₃). COOC₂H₅, and benzoyl acetic ester. The methods 3 and 5 are employed in its preparation.

Nascent hydrogen converts it into phenylmethyl carbinol. Chromic acid oxidizes it to benzoic acid, and potassium permanganate to phenyl-

glyoxylic acid.

Acetophenone, like acetone, has been introduced into numerous nucleus-synthetic reactions. Some of the simplest of these will be given. It may be condensed to dypnone (see this) and to [1,3,5] triphenylbenzene, two bodies bearing the same relation to acetophenone that mesityl oxide and mesitylene sustain to acetone.

Acetophenone also condenses in the most varied proportions with benzaldehyde, forming benzalacetophenone, benzaldiacetophenone, and dibenzal-triacetophenone (B. 29, 1488). It yields the nitrile of a phenyllactic acid with hydrocyanic acid. At higher temperatures chlorine enters the methyl group; PCl₅ substitutes the ketone-oxygenproducing acetophenone chloride (A. 217, 105). Amyl nitrite and sodium ethylate convert acetophenone into isonitrosoacetophenone, which will be described under Phenylglyoxal.

Ortho-ethers of Acetophenone, like Acetophenone Ortho-ethyl Ether, C₆H₅C-(OC₂H₅)₂CH₃, boiling at 107° (17 mm.), are prepared from acetophenone and ortho-formic ethers (1, 233) (B. 29, 2932). When heated under ordinary pressure they lose alcohol and pass into alkyl ethers of phenylolefine alcohols. They yield anils with aniline: Acetophenone-anil, CaHaC: (NCaHa)CHa, melts at 41° and boils at 310°.

Acetophenone Oxime, C₆H₅. C: (N. OH). CH₃, melts at 59°. It is only known in one modification (B. 24, 3482). By the action of concentrated sulphuric acid, or of HCl in glacial acetic acid, it is converted into acetanilide, C₆H₅. NH. CO. CH₅ (p. 82). This remarkable intramolecular atomic rearrangement was discovered by Beckmann (Beckmann's Transposition, B. 20, 2580; 23, 2746).

Other ketoximes behave in an analogous manner. The reaction has been applied in determining the point of double union in the higher olefine monocarboxylic acids (1, 284), and for the decomposition or rupture of

ring ketones.

Acetophenone Phenylhydrazone melts at 105°.

Acetophenone Homologues.—These are numerous and can be arranged in two groups: A. Ketones whose CO-group is attached to the benzene ring: acidylated benzenes. B. Ketones whose CO-group is not in immediate union with the benzene ring: phenylated fatty ketones.

A. Acidylated benzenes have been made especially by the general methods 3, 5, 6, and 7 (p. 188). At first some of the ketones were considered as benzoyl-paraffins and cycloparaffins, and others as homobenzoylated paraffins:

Propiophenone, Propionyl Benzene, boils at 210°; its oxime melts at 53° and boils

230°. 240°. 230°. 155° (15 mm

```
Laurobenzene, C<sub>6</sub>H<sub>5</sub>CO. C<sub>11</sub>H<sub>22</sub>, melts at 47° (B. 28, R. 648).
Palmityl Benzene, C<sub>6</sub>H<sub>5</sub>. CO. C<sub>15</sub>H<sub>21</sub>, melts at 59° and boils at 251° (15 mm.).
```

Palmityl Benzene, Calib. Co. CH2 CH2

Benzoyl Trimethylene, CaH4CO. CH<
CH2

CH2 acetic acid to 200°, boils at 239°. Its oxime melts at 88°.

Benzoyl Tetramethylene, C₈H₈COCH<CH₂>CH₂, from the chloride of tetramethy-

lene carboxylic acid, boils at 258° (B. 25, R. 372).

Nucleus-acidylated Alkyl Benzenes, homobensoylated Paraffins. -p-Acetyl toluene is produced when concentrated nitric acid acts upon cymene (p. 56), and acetyl-3,4-(0) xylene is formed from camphor by the action of concentrated sulphuric acid (B. 26, R. 415):

```
p-Acetyl Toluene, CH3CO[4]. C6H4[1]. CH3, boils at 224°.
                                               246°.
1-Acetyl-3,4-(0)-xylene, . . . . . . . . . . . . .
                                                247°.
I-Acetyl-2,4-(m)-xylene, . . . . . . . . . . . .
 "
                                                224°.
                                           "
                                                235° (B. 24, 3542).
1-Acetyl-2,4,5,6-durene, . . . melts at 73° and
                                                260° (B. 29, 847).
```

B. Phenylated Fatty Ketones have been prepared by methods 3, 4, and 6 (p. 188):

```
Benzyl Acctone, CaHaCHa. CHa.CO. CHa, . . . . . . . .
                                 235° (B. 14, 889).
```

Substituted Acetophenones: Haloid acetophenones. Acetophenones containing halogens in the methyl group will be discussed after the corresponding oxygen derivatives: benzoyl carbinol (see this), phenyl glyoxal (see this), and phenylglyoxylic acid (see this). p. Haloid acetophenones, like Cl. CaH4. CO. CH3, have been obtained from haloid benzenes, acetyl chloride, and aluminium chloride (compare haloid thiophene ketones) (B. 24, 997, 3766):

- p-Chloracetophenone, Acetyl-p-chlorbenzene, melts at 20° and boils at 230° (B. 18, R. 502).
- p-Bromacetophenone, Acetyl-p-brombenzene, melts at 51°.
- p-Iodacetophenone, Acetyl-p-iodbenzene, melts at 83°.

Nitro-acetophenones. — The meta-body is the chief product (just as in the case of benzaldehyde) when acetophenone is dissolved in fuming nitric acid; at 30-40° o-nitroacetophenone predominates (B. 18, 2238). The three isomerides can be prepared from the three nitrobenzoyl-acetoacetic esters (see these) (A. 221, 323).

p-Nitroacetophenone is formed when concentrated sulphuric acid acts upon p-nitrophenylpropiolic acid (see this), through the rearrangement of the nitrophenylacetylene, formed at first, by water (A. 212, 160) (see method of formation 2, p. 188).

o-Nitro-acetophenone is an oil of peculiar odor.

m-Nitro-acetophenone melts at 93°, and its oxime at 131° (B. 15, 3063).

p-Nitro-acetophenone melts at 80°.

Amido-acetophenones, C6H4(NH2). CO. CH3.

o., m., and p. Amido-acetophenone are obtained: By reducing o-nitroacetophenone (A. 221, 326); from o-amido-phenyl acetylene, CaH₄(NH₂)C; CH, by the action of sulphuric acid (B. 17, 964); by boiling o-amidophenyl-propiolic acid with water (B. 15, 2153); and a slight quantity on heating aniline with acetic anhydride (B. 18, 2688). o-Amidoacetophenone is a thick, yellow oil, which boils at 242-252°, and possesses a characteristic sweetish odor. m-Amido-acetophenone melts at 93°. p-Amidoacetophenone melts at 106°; its oxime melts at 147° (B. 20, 512). A pine splinter dipped into the aqueous solution of o-amidoacetophenonehydrochloride is colored an intense orange-red.

Hetero-ring Formations of the Aromatic o-Amido-Ketones.

Dimethyl quinoline is produced (B. 19, 1037) when o-amidoacetophenone is digested with acetone and sodium hydroxide. Oily nitro-compounds are formed in the nitration

of phenylacetone (p. 190) and benzylacetone. They yield, by reduction, β -methyldihydro-ketol and tetrahydroquinaldine (B. 14, 889), as the o-amido-bodies (probably the o-amido-alcohols) produced at first sustain an intramolecular anhydride formation:

$$\begin{array}{lll} C_{0}H_{4} & C_{0}H_{4} & C_{0}CH_{3} & C_{0}H_{4} & C_{0}CH_{3} & C_{0}H_{4} & C_{0}CH_{3} & C_{0}H_{4} & C_{0}CH_{3} & C_{0}CH_{3}$$

Acetophenone Sulphonic Acid, SO₂H. C₂H₄. CO. CH₃ (B. 19, 2626).

4. AROMATIC MONOCARBOXYLIC ACIDS.

The aromatic carboxylic acids result upon replacing the hydrogen in benzene or its homologues by the carboxyl group. This group in these new derivatives is directly linked, as in the benzene carboxylic acids, to the benzene ring or it replaces the hydrogen of a side-chain:

Only the mono-carboxylic acids will be now discussed, after the mono-hydric aromatic alcohols.

General Methods of Formation.—(1) While the aliphatic monocarboxylic acids or the paraffin carboxylic acids could not be obtained by the oxidation of the paraffins, the aromatic acids can be readily obtained from the benzene homologues by oxidizing the side-chains to carboxyl groups. The importance of this reaction in establishing constitution has been previously alluded to (p. 52). The most suitable oxidants are chromic acid, dilute nitric acid, potassium permanganate, and potassium ferricyanide.

(a) Oxidation with Chromic Acid.—Only the para- and meta-derivatives (the former more readily than the latter) of benzenes, carrying two side-chains, are oxidized to acids by chromic acid, while the ortho- are either not attacked at all or are completely destroyed.

In substituted alkyl benzenes the alkyl-group is prevented from being oxidized by chromic acid, if a negative group occupying the o-position with reference to the alkyl-group is present (B. 15, 1021). The oxidations are conducted either with free chromic acid in glacial acetic acid, or with a mixture of potassium bichromate (3 parts) and sulphyric acid (2 parts), diluted with 2-3 volumes of water.

phuric acid (3 parts), diluted with 2-3 volumes of water.

(b) Oxidation with Nitric Acid.—When oxidizing with nitric acid use acid diluted with 3 parts of water and boil for some time, in connection with a return condenser (2-3 days). Konowaloff (p. 178) contends that phenylnitroparaffins are first produced; these then are further oxidized to carboxylic acids. To remove the nitro-acids which are invariably formed, the crude product is digested with tin and concentrated hydrochloric acid; this converts the nitro- into amido-acids, which dissolve in hydrochloric acid.

In the derivatives with two different alkyls the higher alkyl is usually attacked first, by nitric acid or chromic acid; sometimes ketones are present in the intermediate (see Company p. 56)

(see Cymene, p. 56).

(c) Potassium permanganate often effects the oxidation at ordinary

Ortho diderivatives may also be subjected to oxidation, without having the complete de-

struction of the benzene nucleus follow as a consequence.

(d) Potassium ferricyanide oxidizes methyl to carboxyl, if the nitro-group occupies the ortho-position relatively to the methyl-group. This does not occur if the nitro-group holds the meta-position (B. 22, R. 501).

- (2) Oxidation of the corresponding aromatic alcohols and aldehydes.
- (3) By the addition of hydrogen to the unsaturated monocarboxylic acids. Cinnamic acid becomes hydrocinnamic acid.
- (4) By the reduction of phenylated oxyfatty acids, haloid aromatic acids, and ketone carboxylic acids.

1.
$$C_6H_5 \cdot CH_3 \longrightarrow C_6H_5 \cdot COOH$$

2. $C_6H_5 \cdot CH_2OH \longrightarrow C_6H_5CHO \longrightarrow C_6H_5 \cdot COOH$
3. $C_6H_5 \cdot CH = CH \cdot COOH \xrightarrow{2H} \longrightarrow C_6H_5 \cdot CH_2 \cdot CH_3 \cdot COOH$
4. $C_6H_5 \cdot CH(OH) \cdot COOH \xrightarrow{2HI} \longrightarrow C_6H_5 \cdot CH_2 \cdot COOH$
 $C_6H_5 \cdot CO \cdot CO_2H \xrightarrow{4HI} \longrightarrow C_6H_5 \cdot CH_2 \cdot COOH$
 $C_6H_5 \cdot CHCI \cdot COOH \xrightarrow{2H} \longrightarrow C_6H_5 \cdot CH_3 \cdot COOH$

Nucleus-synthetic Reactions:

- (5) Action of sodium and CO₂ upon monobrombenzenes (Kekulé).
- (6) A similar reaction is that of sodium and esters of chlorcarbonic acid upon phenols and bromhydrocarbons (Wurtz).
 - (7) Fusion of salts of the sulphonic acids with sodium formate.
- (8) The action of phosgene gas upon benzenes in the presence of aluminium chloride; at first acid chlorides are produced.
- (9) Urea chlorides, in the presence of AlCl₃, act in an analogous manner upon the benzenes. Acid amides are the first products. The urea chlorides can be replaced by cyanuric acid, by nascent cyanic acid, and by carbanile.

(10) By the synthesis of the acid nitriles—

- (a) upon fusing the sulphonates with potassium cyanide:
- (b) by action of potassium cyanide upon the phenylalkyl chlorides;
- (c) when the bromnitrobenzenes are heated with potassium cyanide;
- (d) when diazo salts are treated with potassium cyanide and copper sulphate;
 - (e) by heating the isonitriles alone.

The nitriles are changed to carboxylic acids when they are heated with mineral acids or alkalies.

Nucleus Syntheses:

(11) Action of benzyl chloride upon sodium acetoacetic ester, and the decomposition of the ketonic esters—e. g., benzyl acetoacetic ester—by alkalies.

(12) The decomposition of phenyl substitution products of the malonic acid series—

r. g., benzylmalonic acid—by heat.

(13) Action of metallic sodium upon the acetates, propionates, etc., of the phenyl carbinols: benzyl acetate yields phenylpropionic benzyl ester and phenylacrylic acid, while benzyl phenyl-butyric ester and phenylcrotonic acid are obtained from benzylpropionate (A. 193, 321; 204, 200):

$$\begin{split} & \overset{COOCH_2.\ C_6H_5}{\overset{4}{\overset{1}{\text{CH}_2}}} + 2\text{Na} = 2 \overset{COOCH_2.\ C_6H_5}{\overset{1}{\overset{1}{\text{CH}_2}}} + 2\overset{CO_2\text{Na}}{\overset{1}{\text{CH}_3}} + H_2 \\ & \overset{CO.\ OCH_2.\ C_9H_5}{\overset{1}{\overset{1}{\text{CH}_3}}} + 2\text{Na} = 2 \overset{COONa}{\overset{1}{\overset{1}{\text{CH}_3}}} + 2\text{C}_6H_5 + 2\text{C}_6H_5\text{CH}_3 + H_3. \end{split}$$

Occurrence, Properties, and Deportment.—The aromatic acids occur naturally, partly in a free state, partly in many resins and balsams, and in the animal organism (see benzoic acid). They arise also in the decay of

albuminoid bodies (see hydrocinnamic acid) (B. 16, 2313).

The aromatic acids are crystalline solids, which generally sublime undecomposed. Most of them dissolve with difficulty in water, hence are precipitated from their salt solutions by mineral acids. Sodium amalgam or zinc-dust will reduce some to aldehydes, and heating with concentrated hydriodic acid or phosphonium iodide converts them into hydrocarbons. When heated with lime or soda-lime, their carboxyl-groups are eliminated and hydrocarbons result (compare methane, 1, 80).

From the polycarboxylic acids we obtain, as intermediate products, acids having fewer carboxyl groups—e. g., phthalic acid first yields ben-

zoic acid and then benzene.

The hydrogen of the benzene nucleus in the acids can sustain substitutions similar to those observed with the hydrocarbons and phenols by the halogens, and the groups NO₂, SO₃H, NH₂, OH, etc. In other respects they are very similar to the fatty acids, and afford corresponding derivatives by the alterations of the carboxyl group.

Benzoic Acid, Phenyl Formic Acid, C₆H₅. COOH, melting at 120° and boiling at 250°, occurs free in some resins, especially in gum benzoin (from Styrax benzoin), in dragon's blood (from Damonorops Draco), also in Peru and tolu balsams, where it exists in the form of its benzyl

ester. It is found as hippuric acid in the urine of herbivoræ.

It is produced by the general methods 1 and 2 (pp. 191, 192) from toluene, benzyl alcohol, and benzaldehyde upon oxidation, as well as from all hydrocarbons, alcohols, aldehydes, ketones, and carboxylic acids and their derivatives, which are obtainable from benzene by the replacement of one hydrogen atom by a univalent side-chain. Benzoic acid can also be prepared by the oxidation of pure benzene; this is very probably due to the oxidation of diphenyl, which is formed at first (A. 221, 234). Toluene can also be changed to benzyl chloride, and this then be oxidized (see preparation) to benzoic acid, or benzotri-chloride may be heated with water, concentrated sulphuric acid, or anhydrous oxalic acid, and the product will be benzoic acid. It can also be obtained, by the nucleus-synthetic reactions 5 and 10, from benzene,

brombenzene, sodium benzene sulphonate, and from aniline through diazobenzene chloride or phenylcarbylamine (p. 193). Finally, CO, can be added to benzene by means of aluminium chloride, and benzoic acid will result.

History.—Benzoic acid was obtained from gum benzoln by sublimation, in the beginning of the 17th century. In 1775 Scheele showed how the acid could be extracted from the gum with lime-water, and then be precipitated from the solution of its calcium salt. In 1832 Liebig and Wöhler, in the course of their classic research upon the radical benzoyl, determined the elementary composition of the acid and illustrated its connection with benzaldehyde, as well as pointed out the simplest transformation products of the acid. This investigation produced such a profound impression upon the great master, Berzelius, that he proposed as a substitute for the name benzoyl—the name of the new radical containing more than two elements—that of proin or orthrin, from the Greek words, $\pi\rho\omega$, the beginning of day, or $\delta\rho\theta\rho\rho\sigma$, morning dawn, because a new day was now breaking for organic chemistry. In 1834 Mitscherlich distilled benzoic acid with lime and got benzene, which led him to regard the acid as a derivative of this hydrocarbon. From that day, and especially since the establishment of the benzene theory by Aug. Kekulé, benzoic acid has been serving in constantly increasing amount as the starting out material for the preparation of innumerable products. It is the acid which has been most exhaustively investigated. The study of its derivatives has been greatly facilitated by the fact that the great crystallizing power of the acid has been transferred to most of its compounds (1, 271).

Preparation.—Gum benzoin is sublimed or the resin is boiled with milk of lime, and the benzoic acid precipitated with hydrochloric acid. A more advantageous method is the production of the acid from hippuric acid. To accomplish this, boil the latter with concentrated hydrochloric acid. It is also produced when benzyl chloride is boiled with dilute nitric acid (B. 10, 1275). Benzoic acid results from phthalic acid by heating its

calcium salt to 350° with calcium hydroxide.

Properties and Deportment.—Benzoic acid crystallizes from hot water, in which it is very soluble, in white, shining leaflets. It sublimes readily, and is carried over with steam. It dissolves with difficulty in cold water (1 part in 600 parts at 0°). Its vapors possess a peculiar odor, which produces coughing and sneezing. The officinal benzoic acid is obtained by the sublimation of Siam gum benzoin.

The acid yields benzene and carbon dioxide when heated with lime. Benzoic acid, upon reduction, can yield tetra- and hexa-hydrobenzoic acids

(see these).

Salts.—The benzoates are mostly quite readily soluble in water. Ferric chloride throws

out a reddish precipitate of ferric benzoate from their neutral solutions.

The potassium salt, 2C₇H₅KO₂ + H₂O₃ crystallizes in concentrically grouped needles. The calcium salt, (C₇H₅O₂)₂Ca + 3H₂O₃ consists of shining prisms or needles. The silver salt, C₇H₅AgO₂, crystallizes from hot water in bright leaflets.

Homologues of Benzoic Acid.—These compounds, like the homologues of benzaldehyde and acetophenone, can be arranged into two groups: alkyl bensoic acids, in which the CO₂H-group is attached to the benzene nucleus, as in benzoic acid itself, and phenyl fatty acids, in which the carboxyl group occurs in an aliphatic side chain of an alkyl benzene. The first group or class is naturally more nearly related to benzoic acid than the second group.

Alkyl Benzoic Acids - Toluic acids or monomethyl benzoic acids, CH3 . C4H4 . CO4H, are isomeric with a toluic acid or phenylacetic acid (p. 196). They are produced when the three xylenes are boiled for some time with dilute nitric acid, and from brom and iod-toluene, by the nucleus-synthetic methods 5 and 6, as well as from the three tolu-

idines according to method 10.

o-Toluic acid can also be obtained by the reduction of phthalide with hydriodic acid (B. 20, R. 378), as well as by rupturing the ring of 1,3-naphthalene derivatives, like 1,3-dioxynaphthalene, 1,3-naphthalene disulphonic acid, 1,3-naphthol sulphonic acid upon fusing them with caustic alkali (B. 29, 1611). p-Toluic acid is formed on boiling cymene (p. 56) with dilute nitric acid.

```
o-Toluic acid melts at 102°.
m-Toluic acid " " 110° and boils at 263°.
p-Toluic acid " " 180° " " 275°.
```

Ethyl Benzoic Acids, C₂H₅. C₆H₄. CO. OH.—The three isomerides are known. The o-acid results in the reduction of o-acetophenone carboxylic acid, of methyl phthalide

(B. 29, 2533), and of phthalyl acetic acid, C_6H_4 $\begin{cases} C = CHCO_2H \\ > O \end{cases}$, with hydriodic acid C_0

(B. 10, 2206), and in that of the chlorvinylbenzoic acids with sodium amalgam (B. 27, 2761).

o, m-, and p-Ethyl Benzoic Acids melt at 68°, 47°, and 112° (B. 21, 2830; A. 216, 218) respectively.

Dimethyl Benzoic Acids, (CH₃)₂C₄H₃CO₂H.—Mesitylenic acid is the most important member of this group. It is formed when mesitylene, symmetrical or [1,3,5]-trimethyl benzene (p. 55), is oxidized with dilute nitric acid. Isoxylene or m-xylene is obtained when this acid is distilled with lime. These reactions are the basis of the evidence that isoxylene (p. 54) and its oxidation products, m-toluic acid and isophthalic acid, are m-disubstitution products of benzene (p. 37). Further oxidation of mesitylenic acid leads to uvitic acid and trimesic acid.

```
      1,2-Dimethyl-3-benzoic Acid,
      a-Hemellitic Acid, melts at 144° (B. 19, 2518).

      1,2-Dimethyl-4-benzoic Acid,
      p-Xylic Acid,
      " 163° (B. 17, 2374).

      1,3-Dimethyl-2-benzoic Acid,
      " 98° (B. 11, 21).

      1,3-Dimethyl-4-benzoic Acid,
      " 126° (B. 12, 1968).

      1,3-Dimethyl-5-benzoic Acid,
      " 166° (A. 141, 144).

      1,4-Dimethyl-2-benzoic Acid,
      Isoxylic Acid,
      " 132°; boils at 268°

      (A. 244, 54).
```

Propyl Benzoic Acids, C₅H₇. C₆H₄CO₂H.—o- and p-n-Propyl and p-isopropyl benzoic acids are known. p-Isopropyl benzoic acid, or *cumic acid*, the oxidation product of cuminic alcohol (p. 184) (B. 11, 1790), is deserving of the most note. Cumic acid is further produced by the oxidation of cymene (p. 56) in the animal organism, as well as by the rearrangement of *nopic acid* which results from the oxidation of turpentine oil (B. 29, 1927). Chromic acid oxidizes cumic acid to terephthalic acid, and potassium permanganate converts it into p-oxyisopropyl benzoic acid and p-acetyl benzoic acid:

```
o,n-Propylbenzoic acid melts at 58° (B. 11, 1014).
p,n-Propylbenzoic acid melts at 138° (B. 21, 2231).
o-Isopropylbenzoic acid melts at 51° (A. 248, 63).
```

Cumic Acid, p-Isopropyl Benzoic Acid, melts at 117° (A. 219, 279; B. 26, 860).

Trimethyl Benzoic Acids.—Five are known. Durylic acid is obtained from durene, and a-, β -, and γ -isodurylic acids from isodurene (B. 27, 3446), upon oxidation with

dilute nitric acid. β -Isodurylic acid or mesitylene carboxylic acid can also be formed from acetyl mesitylene (p. 190) (B. 25, 503):

```
1,2,3·Trimethyl-4-benzoic Acid, Prehnitylic Acid, melts at 167°.
1,2,3·Trimethyl-5-benzoic Acid, a-Isodurylic Acid, " 215°.
1,2,4·Trimethyl-6-benzoic Acid, Durylic Acid, " 150°.
1,2,4·Trimethyl-6-benzoic Acid, β-Isodurylic Acid, " 127°.
1,3,5·Mesitylene Carboxylic Acid, β-Isodurylic Acid, " 152°.
```

Tetramethyl Benzoic Acids.—Several are known: 1,2,3,4-Tetramethyl-5-benzoic acid, melting at 165°, is the oxidation product of pentamethyl benzene (B. 20, 3287); 1,2,3,5-Tetramethyl-6-benzoic acid, durene carboxylic acid (B. 29, 2569); 2,3,5,6-Tetramethyl Benzoic Acid melts at 127° (B. 29, R. 233).

Pentamethyl Benzoic Acid, (CH₃)₅. C₄. CO₂H, melting at 210°,

is made according to method 8 (B. 22, 1221).

Phenyl Fatty Acids.—The most important representatives of this group are phenylacetic acid or α-toluic acid, β-phenylpropionic acid or hydrocinnamic acid, and α-phenylpropionic acid or hydratropic acid. The synthesis and decomposition of the phenyl fatty acids can be realized in the same manner as the synthesis and decompositions of the fatty acids (1, 251). The general methods of formation 2, 3, 4, 106, 11, 12, and 13 (pp. 191, 192) are particularly prominent in the formation of the phenyl fatty acids.

Phenyl-acetic Acid, Alphatoluic Acid, C₆H₅. CH₄. CO₂H, melts at 76° and boils at 262°. This acid is formed from toluene just as acetic acid is obtained from methane. Toluene is converted into benzyl chloride, and this into benzyl cyanide (method 106, p. 192), which is then digested with sulphuric acid (B. 19, 1950; 20, 592):

$$\begin{array}{ccc} \text{CH}_{4} - & \longrightarrow & \text{CH}_{3}\text{CI} & \longrightarrow & \text{CH}_{3}\text{CN} \longrightarrow & \text{CH}_{3}\text{. CO}_{2}\text{H}. \\ \text{C}_{6}\text{H}_{5}\text{. CH}_{3} \longrightarrow & \text{C}_{6}\text{H}_{5}\text{. CH}_{2}\text{CI} \longrightarrow & \text{C}_{6}\text{H}_{5}\text{. CH}_{2}\text{CN} \longrightarrow & \text{C}_{6}\text{H}_{6}\text{. CH}_{2}\text{. CO}_{3}\text{H}. \end{array}$$

It can also be obtained from phenyl chloracetic acid, C₆H₅. CHCl. CO₂H (B. 14, 240), from phenyl glycollic acid or mandelic acid, C₆H₅CH-(OH). CO₂H, and phenylglyoxylic acid, C₆H₅. CO. CO₂H, by reduction.

It is produced when phenylmalonic acid is heated (see method 12, p. 193), and it appears in the decay of albuminates (B. 12, 649). It may be prepared, furthermore, from brombenzene, chloracetic ester, and copper (B. 2, 738), and by heating acetophenone with yellow ammonium sulphide (B. 21, 534). Chromic acid oxidizes it to benzoic acid. Chlorine, in the heat, converts it into phenylchloracetic acid, while in the cold the halogens replace the aromatic hydrogen.

Tolyl-acetic Acids, Alpha-xylic Acids, $C_6H_4 < \frac{CH_8}{CH_3}$. CO_3H .—The three isomeric acids have been obtained from the three xylene bromides. The ortho-acid melts

at 89°, the meta at 61°, and the para at 91° (B. 20, 2051; 24, 3965).

The esters of two acids, isomeric with phenyl- and tolyl-acetic acids, result from the action of diazo-acetic ester (1, 365) upon benzene and toluene. These acids have been called pseudophenyl-acetic acid (the amide melts at 141°) and pseudophenyl-acetic acid. The only product formed in any appreciable amount by the oxidation of pseudophenyl-acetic acid is terephthalic acid. The constitution of this body has never been explained. It has been assumed that it contains the residue =CH. COOH, attached to two carbon atoms of the nucleus (B. 29, 106, 632).

Hydrocinnamic Acid, β-Phenylpropionic Acid, C₆H₅. CH₂. CH₁. CO₂H, melting at 47° and boiling at 280°, is isomeric with a-phenylpropionic acid, the three alphaxylic acids, the three ethylbenzoic acids, and the six dimethylbenzoic acids. It is obtained: by the action of sodium amalgam upon cinnamic acid, or β-phenylacrylic acid, or hydriodic acid (B. 13, 1680); from phenylethyl cyanide (A. 156, 249); from benzyl acetoacetic ester (B. 10, 758) and benzyl malonic ester (A. 204, 176); also from benzyl acetic ester with sodium (A. 193, 300) (see, further, methods 11, 12, and 13); and in the decay of albuminoid substances (B. 12, 649). Chromic acid oxidizes it to benzoic acid.

The aliphatic baloid hydrocinnamic acids, readily obtained by the addition of haloid acids and halogens to cinnamic acid, will be described after phenyllactic and phenylglyceric acids.

Hydratropic Acid, α-Phenyl-propionic Acid, C₆H₅CH(CH₃). - CO₂H, boiling at 265°, is an oil, volatile in aqueous vapor. It results from the reduction of atropic acid or α-phenylacrylic acid, C₆H₅-C(=CH₂). CO₂H, and in the action of hydriodic acid upon the prussic acid addition product of acetophenone—the nitrile of atrolactinic acid (A. 250, 135).

Higher homologues of these acids are usually made according to the following reactions: (1) By reduction of homologous cinnamic acids (see these), which can be readily prepared by Perkins' reaction from the aromatic aldehydes. (2) By the reduction of homologous mandelic acids, obtained from homologous phenylglyoxylic acids. The latter result upon oxidizing homologous acetyl benzenes with potassium permanganate. (3) From alkylized benzyl cyanides, which are produced by the action of alkylogens upon sodium benzyl cyanide.

γ-Phenyl-butyric Acid, C₈H₅. CH₂. CH₂. CH₄. COOH, melting at 51.7°, is formed by the reduction of phenylbutyrolactone. δ-Phenyl-valeric Acid, C₈H₅(CH₂)₄COOH, melting at 59°, results from the reduction of phenyl coumalin (see this) with hydriodic acid (B. 29, 1675, R. 14).

DERIVATIVES OF THE AROMATIC MONOCARBOXYLIC ACIDS.

The derivatives of benzoic acid and its homologues arrange themselves into two groups. The first group comprises those compounds resulting from the alteration of the carboxyl group (see Acetic Acid, 1, 222, 223), and the second group the aromatic substitution products with the exception of the phenol monocarboxylic acids. The first group divides itself into A, the benzoyl compounds; B, the benzenyl compounds and the derivatives of orthobenzoic acid. The chemistry of no single carboxylic acid has been so richly developed as that of benzoic acid.

A. BENZOYL COMPOUNDS.

1. Esters of the Monobasic Aromatic Acids (1, 254).—The benzoic esters of the alcohols and phenols can be prepared like the acetic esters. Like the latter, they are frequently employed in determining the number of alcoholic hydroxyl groups present in a compound. They are made (1) by the action of hydrochloric acid upon an alcoholic solution of benzoic acid; (2) by the action of benzoyl chloride or benzoic anhydride upon alcohols, alcoholates, phenols, and phenolates; (3) by the action of alkylogens upon salts,

usually the silver salts. In carrying out the second reaction it is advisable to gradually add sodium hydroxide, and shake the alkaline, aqueous solution of the alcohols with benzoyl chloride until there is a permanent alkaline reaction (Baumann, B. 19, 3218). In this manner, also, the benzoyl ethers of the polyalcohols, the polyoxyaldehydes, -e. g., of the glucoses,—have been obtained, and nearly all have been completely benzoylated (B. 22, R. 668).

Methyl Benzoic Ester boils at 199°. The ethyl ester boils at 213°; the n-propyl ester at 229°; the n-butyl ester at 247°. Glycol Dibenzoate melts at 73° (B. 23, 2498). tilycerol Tribenzoate melts at 76° (B. 24, 779). Erythrol Tetrabenzoate melts at 187°.

Mannitol Hexabenzoate melts at 124°. Glucose Pentabenzoate melts at 179°.

Benzoyl Glycollic Acid, CaHaCO.OCHa.CO3H, consists of large prisms. It results when nitrous acid acts upon hippuric acid. Phenyl Benzoic Ester melts at 71° and boils at 314° (A. 210, 255; B. 24, 3685). The benzyl ester melts at 20° and boils at 314° (A. 210, 255; B. 24, 3685). 323° (B. 20, 647). It occurs in Peru balsam (A. 152, 130). See pp. 147, 160, and 163

for the benzoyl compounds of the homologous phenols.

The 2,6- and 2,4,6-substituted benzoic acids, like mesitylene carboxylic acid, 2,6dibrom-, and 2,4,6-tribrom-, 2,4,6 trinitrobenzoic acids, etc., are not converted into esters when treated with alcohol and hydrochloric acid. The acids not esterified in this way are quite readily changed to esters by the interaction of alkylogens and the silver salts (B. 28, 1468; 29, 1399; compare 29, 2301).
2. Aromatic Acid Haloids or Haloid Anhydrides of the Aromatic Acids

(1, 257).—The methods pursued in the preparation of these bodies are similar to those

employed for the corresponding fatty derivatives (1, 257).

Benzoyl Chloride, C₆H₆. COCl, melting at —1° and boiling at 198°, is isometic with the chlorinated benzaldehydes, Cl. C₆H₆. CHO. It is a liquid with penetrating It is formed from benzoic acid, phosphorus pentoxide, and hydrochloric acid (B. 2, 80); from benzaldehyde and chlorine; from sodium benzoate and phosphorus oxychloride; and from benzoic acid and phosphorus pentachloride. The action of phosgene and aluminium chloride upon benzene hydrocarbons, and of anhydrous oxalic add upon benzotrichloride (A. 226, 20), are only applicable in the preparation of the chlorides of benzene carboxylic acids.

The history of benzoyl chloride, the first discovered chloride of a carboxylic acid, was given in connection with the fatty acid chlorides (1, 257). Benzoyl chloride is readily accessible and very reactive; it is therefore one of the most frequently used compounds

in various reactions.

o- and m. Toluyl Chlorides boil at 211° and 218° respectively. Phenyl Actyl

Chloride, C₈H₅. CH₂. COCl, boils at 102° (17 mm.) (B. 20, 1389).

Benzoyl Bromide, C₈H₅. COBr, melting about 0° and boiling at 218°, results from the action of phosphorus tribromide upon benzoic acid (B. 14, 2473). Benzoyl iodide, consisting of crystalline leaflets, is produced when potassium iodide acts upon benzoyl chloride (B. 3, 266). Benzeyl fluoride, from benzoyl chloride and AgF, boils at 1450

So far as concerns properties, benzoyl azimide or benzoyl nitride, to be treated later in connection with benzoyl hydrazine, attaches itself to the halogen anhydrides of benzoic

3. Acid Anhydrides (1, 259).—Benzoic Anhydride, (C₈H₈. CO)₂O, melting at 42° and boiling at 360°, is obtained from benzoyl chloride and sodium benzoate or silver benzoate; from benzoyl chloride and benzotrichloride upon digesting them with anhydrous oxalic acid; from benzoyl chloride by means of lead nitrate (B. 17, 1282) or sodium nitrite (B. 24, R. 371), and by the action of concentrated sulphuric acid upon benzotrichloride (B. 12, 1495).

Aceto-benzoic Anhydride breaks down, when heated, into acetic anhydride and ben-

zoic anhydride (B. 20, 3189).

o-Toluic Anhydride melts at 37°. Phenyl-acetic anhydride, (CaH3. CH2. CO),0,

melts at 72° (B. 20, 1391).

4. Acid Peroxides (1, 261).—Benzoyl Peroxide, (CeII, CO), O,, melts at 103° and deflagrates when heated. It is formed from benzoyl chloride and barium peroxide, or from benzoyl chloride, hydrogen peroxide, and sodium hydrate (B. 27, 1511; 29, 1727). as well as from benzaldehyde, acetic anhydride, and sand, upon exposure to the air (B. 27, 1960).

5. Thioacids (1, 261).—Thiobenzoic Acid, C₆H₅.CO.SH, melts at 24°, and results when benzoyl chloride acts upon alcoholic potassium sulphide. When the ethereal solution of thiobenzoic acid is exposed to the air (A. 115, 27) the acid rapidly changes to *Benzoyl disulphide*, $(C_6H_5O)_2S_3$, melting at 138°. *Benzoyl sulphide*, $(C_6H_5O)_2S_3$, melts at 48°, and is obtained when benzoyl chloride acts upon thiobenzoic acid

(2. f. Ch. (1868), 357).

Thionbenzoic Acid, C₆H₅CSOH (A. 140, 236).

Dithiobenzoic Acid, C₆H₅. CS. SH, a heavy, dark violet-red oil, is obtained when C₆H₆. CCl₃ is boiled with alcoholic potassium sulphide (A. 140, 240).

6. Acid Amides (1, 262).— The methods of formation and the deportment of the acid amides have been sufficiently considered in connection with the fatty acid amides. Attention was also called to the fact that the amides of the carboxylic acids could have two constitution formulas. Thus, benzamide has two formulas:

The imido-ethers are derived from the second formula (see silver benzamide). In addition to the methods mentioned under the amides of the fatty acids must be added, in connection with the amides of the benzene carboxylic acids, their formation through the action of aluminium chloride upon aromatic hydrocarbons and urea chlorides (p. 192).

Benzamide, C₆H₅. CO. NH₂, melting at 130° and boiling at 288°, results (1) when benzoyl chloride is acted upon by gaseous or aqueous ammonia, or by ammonium carbonate (see tribenzamide); (2) from benzoic ester and ammonia; (3) by heating benzoic acid

(see tribenzamide); (2) from benzoic ester and ammonia; (3) by heating benzoic acid and ammonium thiocyanate to 170° (A. 244, 50). It crystallizes in pearly leaflets, melts at 130°, and boils near 288°. It is readily soluble in hot water, alcohol, and ether. Sodium Benzamide, C₆H₆CONHNa or C₆H₆C(:NH)ONa, results from the action of metallic sodium upon benzamide dissolved in benzene (B. 23, 3038).

Silver Benzamide, C₆H₅. CO. NHAg or C₆H₅. C(:NH). O. Ag, obtained by precipitating the aqueous solution of benzamide and silver nitrate with a calculated amount of sodium hydroxide, is a white crystalline powder. When digested with ethyl oddied it yields benzimide ethyl ether (B. 22, 1550): a behavior arguing for the LL foriodide it yields benzimido-ethyl ether (B. 23, 1550); a behavior arguing for the II-formula for the silver salt.

Dibenzamide, (C₈H₅CO)₂NH, melting at 148°, is obtained from benzonitrile with concentrated sulphuric acid, or from benzoyl chloride and benzonitrile with aluminium chloride. When distilled under a pressure of 15 mm. dibenzamide breaks down into benzonitrile and benzoic acid (B. 21, 2389). Sodium dibenzamide, (C_aH_bCO)_bNNa, is a shining, white powder. It is formed when sodium acts upon dibenzamide dissolved in xylene.

Tribenzamide, (C₆H₅CO)₃N, melting at 202°, results in the action of benzoyl chloride in ethereal solution upon sodium dibenzamide, and together with benzamide and

dibenzamide when benzoyl chloride acts upon ammonium carbonate (B. 25, 3120).

Benzoyl Chlorimide, C₆H₆CONHCl, melts at 113°. Benzoyl Brominide, C₆H₅.
CONHBr, melts with decomposition at 170°. Methyl and Dimethyl Benzamide,
C₈H₅CON(CH₃)₃, melt at 78° and 41°.

We get Benzanilide, C₈H₅. CO.NH.C₈H₅, Phenyl-benzamide, on mixing aniline
and benzoyl chloride. It can also be made by the action of aluminium chloride (p. 192) upon benzene and carbanile, and upon heating benzophenoxime, (C₆H₅)₂C: N. OH, with concentrated sulphuric acid, acetyl chloride, or glacial acetic acid containing hydrochloric acid, to 100°, or with glacial acetic acid alone to 180° (B. 20, 2581).

When benzanilide is boiled with sulphur it becomes benzenylamidothiophenol or μ-phenylbenzothiazole (p. 153). o-, m-, and p-Bensoyl Toluides, C₈H₅CONH. C₆H₄CH₂, melt at 131°, 125°, and 158°.

Diphenylbensamide, CaHaCO. N(CaHa), melting at 177°, results from diphenylamine and benzoyl chloride, as well as from diphenylures chloride, benzene and aluminium chloride (B. 20, 2119).

Bensoyl Bensylamine, C. H. CO. NH. CH., C. H., melts at 105° (B. 26, 2273).

Methylene-dibensamide, hipparaffin, CH. (NH. CO. C. H.), melting at 221°, is obtained in the oxidation of hippuric acid with PbO, and dilute sulphuric or dilute nitric

acid, and results from formaldehyde, benzonitrile, and hydrochloric acid (B. 25, 311).

Ethidene Dibenzamide, CH₃. CH(NHCOC₆H₆), melts at 204° (B. 7, 159).

Ethylene Dibenzamide, C₆H₆CO. NH. CH₄. CH₅. NH. CO. C₆H₆, melting at 249°. when heated alone or with hydrochloric acid yields ethylene benzenylamidine, benzok acid splitting off at the same time (B. 21, 2334).

Hippuric Aldehyde, C.H. CO. NH. CH. COH (B. 27, 3093). acetal is formed from amido-acetal (1, 316).

Hippuric Acid, Benzoyl glycocoll, CH₂ < NH. CO. C₆H₅, melting at 187°, decomposes at 240° into benzoic acid, benzonitrile, and prussic acid. It occurs in considerable amount in the urine of herbivorous animals, in that of the cow and horse (lanoc, horse, obpou, urine), and in minute quantities in that of man. Benzoic acid, cinnamic acid, toluene, and other aromatic substances, when taken internally, are eliminated as hippuric acid. It can be obtained artificially (1) by heating benzamide with monochloracetic acid; (2) by the action of benzoyl chloride on silver glycocollide (B. 15, 2740), or (3) by adding sodium hydroxide to glycocoll and shaking with benzoyl chloride (B. 19, R. 307), and (4) by heating benzoic anhydride with glycocoll (B. 17, 1662).

History.—Liebig, in 1829, recognized that hippuric acid was a different body from benzoic acid, and to indicate its origin named it hippuric acid. In 1839 he established its constitution. Dessaignes (1846) showed how upon boiling with strong alkalies or acids it was resolved into glycocoll and benzoic acid (J. pr. Ch. [1] 37, 244). In 1848 Strecker converted the acid by means of nitrous acid into benzoyl glycollic acid (A. 68, 54), and in 1853 Dessaignes synthesized hippuric acid from benzoyl chloride and zinc glycocollide (A. 87, 325).

Hippuric acid crystallizes in rhombic prisms, and dissolves in 600 parts cold, and readily in hot water and alcohol. Boiling acids or alkalies decompose hippuric acid into benzoic acid and glycocoll.

Compare hipparaffin (above), benzoylylycollic acid (p. 198), for other transformations of hippuric acid. Hippuric acid condenses with benzaldehyde, sodium acetate and acetic anhydride to benzoylamidocinnamic lactimide (A. 275, 3)

Silver salt, C, H, AgNO3. The ethyl ester melts at 60° (J. pr. Ch. [2] 15, 247). It is converted by PCl₅ (2 mols.) into hippuroflavin, C₆H₅CON:

consisting of citron yellow crystals (B. 21, 3321; 26, 2324). Benzaldehyde and sodium acetate change it to benzoylamidocinnamic ester (A. 275, 12). The phenyl ester melts at 104°. When boiled with POCl3 it passes into anhydrohippuric phenyl ester,

C₆H₅CO. N melting at 42° (B. 26, 2641).

Hippuryl-hydrazine, C₆H₅CO. NH. CH₂. CO. NH. NH₂, melting at 162°, is formed from ethyl hippuric ester and hydrazine. Compare hippuryl-phenyl-buzylene (p. 131) and hippurazide (p. 201) (B. 29, R. 181).

7. Acid Hydrazides (1, 228, 405; 11, 125). Benzoyl Hydrazine, CaHaCO . NHNH2,

melting at 112°, is obtained from benzoic ester and hydrazine. When there is an excess of the ester, sym. Dibensoyl Hydrasine, $(C_0H_5CO\cdot NH)_2$, is formed. This melts at 233° (B. 27, R. 899) (see also benzoylazide, below). Benzoyl Phenylhydrasine, melting at 168° (B. 19, 1203), is converted by mercuric oxide into benzoyl diazobenzene, C_0H_5 . CON₂C₈H₆. This yields an addition product with hydrochloric acid, but it rearranges itself to 0-chlorphenylbenzoylhydrasine (B. 30, 319):

$$C_6H_5CONH \cdot NCl \cdot C_6H_5 \longrightarrow C_6H_5CONHNH[1]C_6H_4[2]Cl.$$

Unsym. Benzoyl-phenylhydrazine melts at 70° (B. 26, 945, R. 816). Dibenzoyl-phenylhydrazine, C₆H₅. CO. N(C₆H₅). NHCO. C₆H₆, melts at 177°.

8. Acidylazides.—Benzoylazide, benzoyl nitride, azimide, C₆H₆CON < N/2, melting

at 20°, is formed when sodium nitrite and acetic acid act upon benzoyl hydrazine (B. 23, 3023). Its odor is intensely like that of benzoyl chloride; it volatilizes in part with aqueous vapor without decomposition, and explodes with slight detonation upon the application of heat. It is insoluble in water, very soluble in ether, and rather readily soluble in alcohol. It reacts neutral. It breaks down, on boiling with alkalies, into benzoic acid and potassium azoimide (B. 23, 3029). Boiling alcohol changes it to phenylurethane, CaHaNH.CO.OC2H5, and nitrogen. Carbanilide and nitrogen result when it is boiled with water. Bromine converts it into nitrogen and a carbanile brom-addition product (J. pr. Ch. [2] 52, 215). The substituted benzoylazides behave similarly. o-, m-, and p-Nitrobenzaziites melt at 36°, 68°, and 69°. The azides can also be obtained by the action of salts of diazo-benzene upon the acid hydrazides. (B. 29, R. 981) (p. 86):

$$C_6H_5CON_8 + C_6II_8CONHNH_9 = N_9 + C_6H_5NHCONH \cdot NHCOC_6H_6$$

Hippurazide, C₆H₅CO. NH. CH₂. CO. N₃, melting at 98°, results when sodium nitrite and acetic acid act upon hippuryl hydrazine. It is decomposed by mineral acids, alkalies, ammonia, and amines, with the elimination of hydrazoic acid. When boiled with alcohols and with water N₂ is evolved, and there result Hippenyl urethane, C₆H₆CONHCH₂NHOOOR, and Dihippenylurea, (C₆H₅CONHCH₂NH)₂CO (B. 29, R. 183).

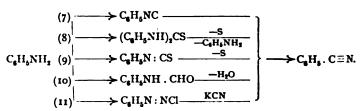
9. Nitriles of the Aromatic Monocarboxylic Acids.—The aromatic nitriles are connected by numerous reactions with the principal classes of the aromatic derivatives. They are produced, like the nitriles of the fatty acids (1, 266), (1) from the corresponding ammonium salts; (2) from the corresponding acid amides by the withdrawal of water with P₂O₅, PCl₅, and SOCl₁ (B. 26, R. 401); (3) by the action of bromine and caustic alkali upon the primary phenylalkylamines; (4) from the aldoximes by the action of acetyl chloride or acetic anhydride. There is also (5) the method of distilling aromatic monocarboxylic acids with potassium sulphocyanide, or, better, with lead sulphocyanide (B. 17, 1766):

$$2C_6H_5 \cdot CO_2H + (CNS)_2Pb = 2C_6H_5CN + 2CO_2 + PbS + H_2S.$$

Nucleus-synthetic Methods.—(6) The direct replacement of the halogens in the benzene hydrocarbons by the cyanogen group is of exceptional occurrence—e.g., when chlor- and brom-benzene are conducted over strongly ignited potassium ferrocyanide, or when benzene iodide is heated to 300° with silver cyanide, the product being cyanbenzene.

However, the phenyl carbinol chlorides—e. g., C₆H₆CH₇Cl—are as readily transposed as the alkylogens into nitriles of the phenyl-fatty acids by means of potassium cyanide.

The nitriles are also intimately related to the anilines, sulphonic acids, and phenols. Thus, aniline yields (7) phenylcarbylamine, which, upon the application of heat, is rearranged into the isomeric nitrile. They are also produced (8) on heating the diphenyl thiureas with zinc-dust; (9) by desulphurizing the phenyl mustard oils with copper; (10) by distilling the formanilides with concentrated hydrochloric acid or with zinc-dust (B. 17, 73); (11) by decomposing diazobenzene chloride with potassium cyanide and copper sulphate.



See p. 38 for the theoretical value of method II.

(12) By distilling the alkali benzene sulphonates with potassium cyanide or yellow prussiate of potash; (13) the distillation of the triphenyl phosphates with potassium cyanide or ferrocyanide; (14) alkyl benzyl-cyanides are formed by the interaction of sodium benzyl cyanide and alkylogens, C_6H_5 . CHNa. CN + $C_2H_5I = C_6H_5$ CH(C_2H_5)CN (p. 203); (15) the hydrogen atoms of the benzenes are directly replaced by the cyanogen group, if cyanogen gas be conducted into the boiling hydrocarbon mixed with aluminium chloride (B. 29, R. 185). Certain nitriles of phenyl-fatty acids occur in the different cresses.

Properties and Deportment.—The benzonitriles are indifferent, agreeably smelling liquids, or solids with low melting points. Their reactions are very numerous, but mention may be made that boiling alkalies or acids convert them into the corresponding aromatic acids, while nascent hydrogen, best from alcohol and sodium, changes them to primary amines.

They yield amide iodides with hydriodic acid.

They combine with alcohols and HCl to form imido-ethers, with ani-

lines to amidines, and with hydroxylamine to amidoximes.

Benzonitrile, Cyanbenzene, C₆H₅. CN, boiling at 191°, with sp. gr. 1.023 (0°), is isomeric with phenyl carbylamine (p. 83), and is best obtained from benzene sulphonic acid by method 12, or from benzoic acid by method 5. It is an oil with an odor resembling that of oil of bitter almonds.

When it is dissolved in fuming sulphuric acid or boiled with sodium, benzonitrile polymerizes to cyanphenine (see this), $C_3N_5(C_6H_5)_5$. Upon nitration the product is almost exclusively m-nitrobenzonitrile (p. 69). For other transpositions see benzimido-ethers and thiobenzamide.

Alphylcyanides: o., m., and p. Tolunitriles, cyantoluenes, $CH_3 \cdot C_6H_4CN$, boil at 203°, 213°, and, 218°. The p-body melts at 29°. p-Xylonitrile boils at 231° (B. 18, 1712). 1, 3-Xylo-4-nitrile melts at 24° and boils at 222° (B. 21, 3082). Cumonitrile, $(CH_3)_2 \cdot CH_{4} \cdot C_6H_{4} \cdot I$] CN, boils at 244°.

Nitriles of Phenyl-fatty Acids: Benzyl Cyanide, Phenylacetonitrile, CaHs. CH, CN, boiling at 232°, with sp. gr. I.014 (18°), is isomeric with the three tolunitriles. It occurs in the ethereal oil of several cresses (Tropzolum majus and Lepidium sativum (B. 7, 1293). It is artificially prepared from benzyl chloride with potassium cyanide. It yields toluic acid by saponification; by reduction β -phenylethylamine (p. 179) is the

product, and upon nitration it is chiefly p-nitrobenzyl cyanide which results.

As in acetoacetic ester and malonic ester, the hydrogen of the CH₂ group, combined with the negative groups C_6H_6 and CN, is very readily replaced. Thus, sodium ethylate produces the mono-sodium derivative, which may be transposed by alkylogens to alkyl benzyl cyanides (see method 14, p. 202) (B. 21, 1291, R. 197; 22, 1238; 23, 2070). Nitrous acid, acting upon a sodium ethylate solution of benzyl cyanide, produces isonitrosobenzyl cyanide (see phenylglyoxalic acid). Sodium ethylate, acting upon benzyl cyanide and benzaldehyde, produces a-phenyl-cinnamic nitrile, C_6H_5 . C(CN): CH. C_6H_5 (B. 22, R. 199).

Methyl Benzyl Cyanides, Tolylacetonitriles, CH₃. C₆H₄. CH₂. CN. The o-body boils at 244°, the meta-body at 241°, while the p-compound melts at 18° and boils at 243° (B. 18, 1281; 21, 1331).

B-Phenylpropionitrile, hydrocinnamic nitrile, C₆H₅CH₂CH₂CN, boiling at 261°

(corr.), occurs in the ethereal oil of spring-cress, Nasturtium officinale (B. 7, 520; B. 26, 1971).

a Phenylpropionitrile, hydratropic nitrile, CaHaCH(CHa)CN, boils at 231° (A. 250,

123, 137).

B. BENZENYL COMPOUNDS.

In addition to the benzonitriles, the classes of bodies from 10 to 26 (p. 209) arrange themselves with the benzenyl derivatives.

10. Amid-haloids. 11. Imide Chlorides. 12. Phenylhydrazide Imide Chlo-

rides (1, 268).

Benzamide Chloride, C₆H₅CCl₂. NH₂(?), results when hydrochloric acid gas is conducted into an ethereal solution of benzonitrile (B. 10, 1891). Benzamide Bromide, phenyldibromformamide, C₆H₅CBr₂NH₂, melts at 70° (A. 149, 307). Benzamide Iodide, phenyldi-iod-formamide, C₆H₅CI₂NH₂, melts with decomposition (B. 25, 2536) at 140°. It is produced when benzonitrile is poured into concentrated aqueous hydriodic acid. Ammonia bases reconvert it into benzoic acid.

Dimethyl Benzamide Chloride, CaH, CCl, N(CH,), from the amide and phosgene,

melts at 36°.

Benzanilid-imide Chloride, C_6H_6CCl ; N. C_6H_5 , melting at 40° and boiling at 310°, is produced when PCl_6 acts upon benzanilide (Wallach, A. 184, 79), or upon benzophenone oxime, $(C_6H_5)_2C=N$. OH, by an intramolecular atomic rearrangement of the chloride, $(C_6H_5)_2C=N$ Cl. Water or alcohol will decompose it into hydrochloric acid and benzanilide. For other transpositions of benzanilide-imide chloride, compare thiobenzalization. anilide, etc.

When benzanilide-imide chloride acts upon sodium acetoacetic ester the products are anil-benzenyl-compounds, β -ketonic acid derivatives, which change to phenyl-quino-

line carboxylic acids upon the application of heat.

Benzphenylhydrasid-imide chloride, CaHaCCl: N. NH. CaHa. melting at 131°, is formed when alcohol acts upon the reaction product of PCl₅ and sym. benzoylphenylhydrazine, C₆H₅. CCl: N. N(C₆H₆)POCl₂ (B. 27, 2122).

13. Imido-ethers of the Aromatic Acids (1, 269). The imido-ethers (their HCl-

salts) result from the action of HCl upon a mixture of a nitrile with an alcohol (Pinner, B.

16, 1654; 21, 2650; 23, 2917).
Water decomposes the HCl-imido ethers into acid esters and ammonium chloride. The following bodies should be viewed as imido-ethers of aromatic carboxylic acids:

$$C_6H_5$$
. $C < O-CH_2$
 $N-CH_2$
 μ -Phenyloxazoline

 $C_6H_5C < O-CH_2$
 $N-CH_2$
 $C_6H_5C < O-CH_2$
 $N-CH_2$
 $C_6H_5C < O[1]$
 C_6H_6
 $C_6H_$

Benzimido-ethyl Bther, C₆H₅. C(NH). O. C₂H₅, is a thick oil, formed by the action of ethyl iodide upon silver benzamide. Its hydrochloric acid salt decomposes at 120° into benzamide and ethyl chloride. The free ether decomposes when heated or upon standing into alcohol and cyanphenine. Ammonia converts it into benzamidine (see this), hydroxylamine into benzamidoxime (see this), and hydrazine into benzamylhydrasidine.

14. Thiamides of the Aromatic Acids.— Thiobensamide, C₆H₅. CSNH₃ or C₆H₅C-(SH)NH, melting at 116°, results on conducting hydrogen sulphide into an alcoholic solution of benzonitrile mixed with ammonia (B. 23, 158), and when benzylamine is heated to 280° with sulphur (A. 259, 304). Zinc and hydrochloric acid convert it into ben-

zylamine (p. 179), iodine into dibenzenylazosulphime (see this), C₆H₅CN—SC. C₆H₅

(B. 25, 1588), ethylene bromide into μ-phenylthiazoline (see below), trimethylene bromide into μ-phenylpenthiazoline (see imido-ethers), and ethylene-diamine into benzenylethylene diamine (see this), C₆H₅C NH—CH₂

Thiobenzanilide, C₆H₅. CSNH. C₆H₅, melting at 98°, consists of yellow plates or prisms. It is formed (1) when H₂S acts upon bearing plantidine at 100°; (2) by

the action of CS, at 110°, hydrosulphocyanic acid being simultaneously produced (A. 192, 29); (3) when H₂S acts upon benzanilide chloride; (4) when P₂S acts upon benzamide; (5) from the interaction of phenyl mustard oil, benzene, and aluminium chloride (B. 25, 3525). It is changed to benzenylamidothiophenol (p. 157) by heat or oxidation

 Imidothio-ethers of the Aromatic Carboxylic Acids are obtained as hydrochlorides from nitriles, mercaptans, and hydrochloric acid (compare imido-ethers). The following compounds must be considered as cyclic imidothio-ethers of benzoic acid:

Benzimidothio-ethyl Ether, C6H5C(NH)S. C2H5, is an oil. It readily resolves itself into benzonitrile and mercaptan (A. 197, 348).

16. Amidines of aromatic monocarboxylic acids (I, 270) are obtained from nitriles, imido-ethers, imide chlorides, and thioamides by means of ammonia and ammonia. nium bases. The cyclic amidines correspond to the cyclic imido-ethers and imidothioethers:

Benzamidine,* Benzenylamidine, C₆H₅. CNH₂, melting at 75-80°, is formed from its hydrochloride, C₇H₈N₂. HCl + 2H₂O, consisting of vitreous crystals, melting at 72°, which anhydrous become liquid at 169° (A. 265, 130).

Silver sall, C₈H₅. C(= NAg)NH₂. Benzamidine is a stronger base than ammonia.

Hydroxylamine converts it, by an exchange of the NH-group for the N(OH)-group, into an amidoxime. Benzamidine gives with diazobenzene : benzamidinediazobenzene (see below); with benzaldehyde: benzalbenzamidine, melting at 175°; with phenylisocyanide: benzenyldiphenyldiurelde, C₆H₅C(: N. CONHC₆H₅). NHCO. NH. C₆H₅, melting at 172°; with phenyl mustard oil: benzamidine phenylthiurea, C₆H₅. C(: NH). NH. CS. NH. C₈H₆, melting at 125°; with chlorcarbonic ester: benzamidine urethane, C₆H₅.-C(: NH). NHCO₂C₂H₆, melting at 58°; heat converts it into diphenyloxycyanudine; with phosgene: dibenzamidine urea: CO(NH. C(: NH). C₆H₅)₂, melting at 289°, and diphenyloxycyanidine.

The action of nitrous acid upon benzamidine is very remarkable. The product is

bensenyldioxytetrazotic acid (see below).

Bensamidine Hetero-ring Formations.—Benzamidine heated alone becomes cyanphenine; heated with acetic anhydride the product is diphenylmethylcyanidine; with trimethylene bromide: trimethylenebensamidine, or \(\mu\)-phenyltetrahydropyrimidine; with acetyl acetone: phenyldimethylpyrimidine; with acetoacetic ester: phenylmethyloxypyrimidine;

Many other amidines besides benzamidine are known; also numerous alkyl-, phenyl-, and benzyl substitution products of the simple amidines. As may be gathered from the description of benzamidine, the amidines are unusually reactive bodies, whose investigation has contributed much to the chemistry of the nitrogen-carbon ring systems. Furfuramidine (see this) deports itself very much the same as benzamidine.

17. Dioxytetrazotic Acids.—Free benzenyldioxytetrazotic acid,

C₆H₅. C N = N. OH (?), is not known. Its benzamidine salt, melting at 178°, is produced when nitrous acid acts upon benzamidine. Sodium amalgam reduces the

produced when nitrous acid acts upon benzamidine. Sodium amalgam reduces the potassium salt to benzenyloxytetrazotic acid, C₁H₆N₄O + H₂O, melting in anhydrous form at 175° with explosion, and benzenyltetrazotic acid (Lossen, A. 263, 73; 265, 129).

These bodies belong to the class of heterocyclic tetrazoles or pyrrotriazoles.

13. Hydrazidines or Amidrazones of aromatic monocarboxylic acids. Several representatives of the aliphatic phenylhydrazidines were discussed in connection with phenylhydrazine. The simple aromatic hydrazidines result from the action of hydrazine upon the imido-ethers. The most thoroughly investigated is—

Benzenylhydrazidine, C₆H₅. C NH. NH₂ or C₆H₅. C NH. NH₂ or C₈H₅. C NH. This compound cannot be obtained from its salts in a pure condition. Its benzoyl derivative, C₈H₅C(:NH)NH.NH.CO.C₆H₅, melts at 188°. It slowly parts with water, even at 120°, changing into c-diphenyltriazole, whereas nitrous acid converts it into dibenzenylisazonime (see this).

In addition to benzenylhydrazidine, produced in the interaction of hydrazine and

benzimido-ether, there also result:

Dibenzenylhydrazidine, C_0H_5 . C(:NH). NH. NH(NH:)C. C_0H_5 or C_0H_5 C(NH_2): $N-N:(NH_2)$ C: C_0H_6 , melting at 202°, and diphenyldihydrotetrazine (see this). Nitrous acid changes benzenylhydrazidine into phenylletrazotic acid (see this).

$$C_{6}H_{5} \cdot C \stackrel{\text{NH} \cdot \text{NH}_{2}}{\text{NH}} \stackrel{\text{Benzenylhydraidine}}{\text{dine}}$$

$$C_{6}H_{5} \cdot C \stackrel{\text{NH} \cdot \text{NH}_{2}}{\text{NH}} \stackrel{\text{NH}_{2} \cdot \text{NH}_{3}}{\text{NH}} \stackrel{\text{Dibenzenylhydraidine}}{\text{dine}}$$

$$C_{6}H_{5} \cdot C \stackrel{\text{NH} - \text{NH}_{2}}{\text{NH}} \stackrel{\text{Cohl}_{3}}{\text{Cohl}} \stackrel{\text{Chiphenyltriazotic}}{\text{Acid}}$$

$$C_{6}H_{5} \cdot C \stackrel{\text{NH} - \text{NH}_{2}}{\text{NH}} \stackrel{\text{Cohl}_{3}}{\text{Cohl}} \stackrel{\text{Chiphenyltriazotic}}{\text{azole}}$$

$$C_{6}H_{5} \cdot C \stackrel{\text{NH} - \text{NH}_{2}}{\text{NH}} \stackrel{\text{Chiphenyltriazotic}}{\text{azole}}$$

Diphenyldihydrotetrazine is readily rearranged by acids into isodiphenyldihydrotetraine. It oxidizes on exposure to the air to diphenyltetrazine (Pinner, B. 27, 3273; 28, 465):

19. Formazyl Derivatives of the Aromatic Monocarboxylic Acids (compare p. 129). Formazyl-benzene, $C_6H_5C_8N = N \cdot C_6H_5$, melting at 173°, consists of red leafets with greenish metallic reflex. It is produced (1) when diazobenzene (p. 129) in alkaline solution (B. 27, 1690) acts upon benzaldehyde-phenyl hydrazone; (2) from benzenyl amidoxime (p. 208) and phenylhydrazine (B. 27, 160); (3) when phenylhydrazine and benzphenylhydrazid-imide chloride (p. 203) interact. The hetero-ring formations of the formazyl compounds have been described (p. 130). A glacial actic acid converts formazyl benzene into phenphenyltriazine (see this). It yields triphenyltetrazolium hydroxide upon oxidation:

$$C_{6}H_{5}.C \bigvee_{N=N+C_{6}H_{5}}^{N=N+C_{6}H_{5}} - \left\{ \begin{array}{c} -C_{6}H_{5}NH_{5} \\ -C_{6}H_{5}C \\ N-N+C_{6}H_{5} \end{array} \right. \bigvee_{N=N-C_{6}H_{5}}^{N=N-C_{6}H_{5}} C_{N} \stackrel{N=N-C_{6}H_{5}}{\longrightarrow} C_{6}H_{5} \\ -C_{6}H_{5}C \bigvee_{N-N+C_{6}H_{5}}^{N=N+C_{6}H_{5}} C_{N} \stackrel{N=N-C_{6}H_{5}}{\longrightarrow} C_{6}H_{5} \\ \end{array} \right. \stackrel{Phenphenyl-triazine}{tetrazolium} Triphenyl-tetrazolium Hydroxide.$$

Guanazyl Benzene, C₆H₅CN. NHC(NH₂): NH, orange-yellow prisms, melting at 199°. It is formed when diazobenzene chloride acts upon benzalamido guanidine, the condensation product derived from benzaldehyde and amidoguanidine (1, 415). Nitric acid oxidizes guanazyl benzene to diphenyl tetrazole (B. 30, 444).

20. Hydroxamic Acids, their Ethers and Esters.—Under benzamide mention was made of the two structural formulas which were theoretically possible for benzamide: the benzamid-formula and the benzimido-acid formula. If we suppose in these formulas an hydrogen atom in union with nitrogen to be replaced by the hydroxyl group, we arrive at the two formulas theoretically possible for an hydroxamic acid:

The amid-formula is preferred for the amides of the carboxylic acids; the imideethers are derived from the imide-acid formula. The oximide-acid formula is, however, more probable for the benzhydroxamic acids. Hydroxime-acid chlorides correspond to the imide-chlorides, and amidoximes to the amidines.

Numerous ethers and esters can be obtained from an hydroxamic acid. accomplished by replacing one or both hydrogen atoms of the CNOH group by alkyl- or acidyl-groups. Although hydroxamic acid and its homologues are known in but one form each, many ethereal derivatives of the hydroxamic acids occur in several similarly constituted modifications, whose demonstrated difference can in no satisfactory way be attributed to structural difference (W. Lossen, A. 281, 169). Just as in the case of the oximes, so here the isomeric phenomena of benzhydroxamic acid ethers are referred to the stereochemistry of nitrogen.

a- and β -Ethylbenzhydroxamic acids differ from each other by the following spaceformulas (Werner, B. 25, 33):

Crystallographic studies have shown that many classes of amide-like derivatives of hydroxylamine appear in polymorphous modifications.

Benzhydroxamic Acid, C₆H₅. C(: NOH). OH, melting at 124°, and Dibenshydroxamic Acid or Benzoylbenzhydroxamic Ester, CaHaC(: NO. COCaHa)OH, melting at 161°, are produced by the interaction of benzoyl chloride and hydroxylamine. The potassium salt of the dibenzhydroxamic acid is decomposed by water, especially on heating, into potassium benzoate, s-diphenylurea, and CO,:

$$2C_6H_5C(:NOCOC_6H_5)$$
. $OK + H_2O = 2C_6H_5COOK + CO(NHC_6H_5)_2 + CO_2$.

The rearrangement occurring here recalls that of the ketoximes (Beckmann, p. 189) to alkylized acid amides. As s-diphenylurea can be resolved by hydrochloric acid into aniline and CO2, it is possible, aided by these reactions, capable of greater generalization, (A. 175, 313; compare benzol axide, p. 201). The alkylethers of dihydroxamic acid are known in two modifications: a-(syn.)-Methyl Ether, melting at 53° ; β -(anti)-Methyl Ether, melting at 55° ; a-(syn.)-Ethyl Ether, melting at 58° ; β -(anti)-Ethyl Ether, melting at 58° ; β -(anti)-Dethyl Ether, melting at δ -(anti caustic potash upon the alkylhydroximic acids.

Benzhydroximic Acid Alkyl Ethers or Alkyl Benzhydroximic Acids, CaHa-C(: NOH)OR', are obtained from benzimido-ethers and hydroxylamine hydrochloride, and from dibenzhydroxamic acid alkyl ethers (A. 252, 211). They occur in two modifications, which can be distinguished by the fact that the a- or syn.-modifications yield in treatment with PCIs (by Beckmann's transposition) phenylcarbamic acid ethers or their transposition products:

$$\begin{array}{c} C_6H_5COCH_3 \\ \\ HON \end{array} \longrightarrow \begin{array}{c} OCOCH_3 \\ \\ C_6H_5 \cdot NH \end{array}$$

whereas the β - or anti-forms become phosphoric ethers of the alkylbenzhydroximic acids (B. 29, 1146). a-(syn.)-Methyl Ether, melting at 64°, readily changes to a physical isomeride; this is also true of the syn.-modification, melting at 101° (B. 29, 1150). β-(anti)- Methyl Ether melts at 44°, a-(syn.)-Ethyl Ether melts at 53°, and β-(anti)-Ethyl

The alkylbenzhydroximic acids also form alkyl and acidyl ethers. Tribenzoyl Hydroxylamine, C₆H₅. C(: NOCOC₆H₅)O. COC₆H₅, is produced in three forms when benzoyl chloride acts upon hydroxylamine hydrochloride: a-modification, melting at 100°; β -modification, melting at 141°; and the γ -modification, melting at 112°. Hydrochloric acid changes the a- and γ -modifications to the β -form (A. 281, 276).

21. Haloids of Benzhydroximic Acid.—The free chlorides, as well as the ethers of the fluorides, chlorides, and bromides, are known. The free chlorides result from the corresponding benzaldoximes upon treatment with chlorine in chloroform solution. The ethers are produced when the amidoxime ethers are treated with haloid acids and an alkaline nitrite; also when PCIs acts upon the alkyl ethers of hydroxamic said (A. 252,

Benshydroximic Acid Chloride, CaHaC(: NOH)Cl, melting at 48°, from benzaldoxime, is converted by ammonia into benzenylamidoxime (B. 27, 2193, 2846). Ben-

doxime, is converted by ambound into benzenylamidoxime (B. 27, 2193, 2240). Benzenyl-methaxime Chloride, C, H, . C(: NOCH,). Cl., boils at 225°, Benzenyl-methaxime Bromide, C, H₅. C(: NOC, H₆) Benzenyl-methaxime acetic Acid, C, H₅. C(: NOCH, . CO, H). OH, melting at 135° to 138°, is formed when caustic potash acts upon benzenylmidraxime-acetic acid, C, H₅. C(: NO. CH, CO₂H)ONO, melting at 95°. The latter is produced through the action of sulphuric acid and potassium nitrite upon benzenylmidoxime-acetic acid (see below). Benzenylfuor-, chlor-, and bromoxime-acetic Acids all melt at 135°. They are obtained when haboid acids and an alkaline nitrite are allowed to not more hemsely. are obtained when haloid acids and an alkaline nitrite are allowed to act upon bensesylamidoxime-acetic acid (B. 26, 1570).

22. The Amidoximes are produced by the action of hydroxylamine upon thioanides, nitriles, imido ethers (p. 203), and amidines (p. 204). Ferric chloride imparts a deep red color to the alcoholic solution of the amidoximes.

Benzenylamidoxime, Amide of Benzhydroxamic Acid, C₆H₈. CN(OH), melts at 79°. It gives the isonitrile reaction with chloroform and potassium hydroxide. Nitros acid changes it to benzemide. With saids and countril in the control of the control acid changes it to benzamide. With acids and caustic alkalies it yields salts-e.g., C_0H_5 . $C(:N.OH)NH_2$. HCl and C_0H_5 . $C(NH_2):N.OK$. Alkyl iodides convertible latter into amidoxime ethers.

Methyl Ether, CaHa(.NHa): NOCHa, melts at 57°; the ethyl ether melts at 67°

(A. 281, 280).

Acctylbenzenylamidoxime, C₆H₅. C(: NOCOCH₃). NH₃, melts at 16° (B. 18, 1082). Benzenyloximidocarbonic Ester, C₆H₄C(. NH₂): NOCO₃C₆H₆, melts at 127°. Benzenyloximidoglycollic acid, C₆H₅. C(. NH₃): NO. CH₂. CO₃H, melts at 123°. Benzenyloxime-butyric acid, C₆H₅C(NH₂): NOCH(C₂H₅)COOH, melts at 82° (B. 29, 2655).

Hetero-ring Formations of the Amidoximes.—(1) The amidoximes condense with the aldehydes of the fatty series to hydrasoximes. The amidoxime acid derivatives, alladed to above, throw off, on heating above their melting points, water or alcohol, and become

asoximes:

23. Aromatic Nitrolic Acids, like CaHs. C(: N.OH)NO2, are not yet known

Derivatives of Orthobenzoic Acid (compare 1, 233). 24. Ethyl Orthobenzoic Ester, Ethyl Orthobenzoste, Bensenylethyl Ether, CaH.

C(O.C.H₅)₃, from phenyl chloroform and sodium ethylate, boils at 220-225°.

25. Benzotrichloride, *Phenylchloroform*, *Benzoic Acid Trichloride*, *Benzenyl Trichloride*, C₆H₅CCl₃, melting at -22.5° (B. 26, 1053), boiling at 213°, with sp. gravity I.38 (14°), is isomeric with the chlorbenzalchlorides, dichlorbenzylchlorides, and the trichlortoluenes. Phenyl chloroform bears the same relation to bensoic acid or phenyl formic acid that methyl chloroform sustains to acetic acid or methyl formic acid (1, 256).

It results (1) upon conducting chlorine into boiling toluene, until there is no further increase in weight (A. 145, 330); (2) by the action of phosphorus pentachloride upon benzoyl chloride (A. 139, 326). It changes to benzoic acid when heated to 100° with water. It yields benzoyl chloride and benzoic anhydride on being digested with anhydrous oxalic acid. It readily condenses to triphenyl methane derivatives with the anilines and phenols (B. 15, 232; A. 217, 223

26. Orthobenzoic Acid Piperidide, C₆H₅C(N. C₈H₁₀)₃, melting at 80°, is produced

on warming benzotrichloride and piperidine.

The bensamide haloids also belong to the derivatives of orthobenzoic acid (p. 203).

SUBSTITUTED AROMATIC MONOCARBOXYLIC ACIDS.

Only those will be given in connection with the monocarboxylic acids in which the substitution has occurred with the hydrogen atoms of the benzene nucleus. Certain ortho-products show the power, by water elimination, of yielding inner anhydrides or heterocyclic compounds.

See p. 197 for the behavior of 2,6-substituted carboxylic acids in their esterification with alcohol and hydrochloric acid.

1. Halogen Benzoic Acids are formed:

(1) By the substitution of benzoic acids or nitriles; the halogen atom entering first prefers the meta-position with reference to carboxyl (p. 69).

(2) By oxidizing p- and m-halogen toluenes and higher homologues with chromic acid, and o-haloid hydrocarbons with dilute nitric acid or

potassium permanganate.

(3) From the amido-acids (a) by means of the diazo-sulphates, or (b)the diazoamido-acids; both classes when boiled with haloid acids yield Thus, the fluor-benzoic acids have been obhaloid carboxylic acids. tained from the diazoamidobenzoic acids (B. 15, 1197).

(4) By the action of phosphorus pentachloride upon the oxy-acids (compare salicylic acid).

(5) Nucleus synthesis: heating the halogen nitrobenzenes to 200-230° with potassium cyanide and alcohol. In this reaction the cyanogen-group replaces the nitro-group; it does not, however, take the same position in the benzene residue (B. 8, 1418). At the temperature of the reaction the nitrile changes to the acid. m-Chlornitrobenzene yields o-chlorbenzoic acid; and p-chlornitrobenzene, m-chlorbenzoic acid.

(6) From the haloid anilines through the diazo-compounds, etc.

Properties and Deportment.—In the following tabulation of the melting points of the mono-haloid benzoic acids it will be observed that the ortho-bodies melt at the lowest temperatures and the para-compounds at the highest. The melting point rises with the atomic mass of the substituting halogen. The ortho-derivatives are rather readily soluble in water, and yield easily soluble barium salts, whereby they can usually be quite readily separated from the meta- and para-derivatives. When they are fused with caustic potash oxy-benzoic acids result.

```
Fluorbenzoic Acid: o-: melts at 118°; m-: melts at 124°; p-: melts at 181°.
Chlorbenzoic Acid: 0: " " 137°; m-: " " 153°; p-: " " 240°.

Brombenzoic Acid: 0-: " " 147°; m-: " " 155°; p-: " " 251°.

Iodbenzoic Acid: 0-: " " 162°; m-: " " 187°; p-: " " 265°.
```

Numerous polychlor- and polybrom-benzoic acids are known. The five hydrogen atoms of the phenyl of benzoic acid can be replaced by chlorine or bromine.

2. Iodoso- and Iodo-benzoic Acids (p. 60).—Upon chlorinating the three 11—18

iodbenzoic acids in chloroform three iodide-chloridebenzoic acids are produced. Sodium hydroxide changes these to the iodoso-benzoic acids (B. 27, 2326). o-lodosobenzoic acids (B, $C_6H_4(10)CO_2H$, consists of brilliant leaflets, which explode at 244°. This acid is also produced in the oxidation of o-iodhenzoic acid with fuming nitric acid (B. 28, 83), and together with o-iodobenzoic acid, C_aH₄(1O₃)CO₂H, exploding at 230° with violence, when o-iodbenzoic acid is oxidized with potassium permanganate. The formula $C_6H_4\left(\begin{bmatrix} 1\\2\end{bmatrix}CO \xrightarrow{} > O \text{ has also been suggested for the o-iodosobenzoic acid, as it yields,} \right)$ like lavulinic acid, when heated with acetic anhydride, an acetyl derivative: acetislusbenzoic acid, C₆H₄ { [1] (OCOCH₃) > 0, melting at 166° (B. 26, 1364).

3. Nitromonocarboxylic Acids.— Not more than three nitrogroups have been introduced into the benzene residue of an aromatic carboxylic acid.

Nitrobenzoic Acids.—(1) Metanitrobenzoic acid is the principal product in the nitration of benzoic acid. The quantity of the ortho (20 per cent.) and para (1.8 per cent.) acids is less (A. 193, 202). (2) By oxidizing the three nitrotoluenes; the ortho with potassium permanganate (B. 12, 443), and the meta and para with a chromic acid misture (A. 155, 25). o- and p-Nitrobenzoic acids are also produced by oxidizing o- and p nitrobenzyl chloride with potassium permanganate (B. 17, 385), as well as by oxidiring of and p-nitrocinnamic acids. (3) By converting the three isomeric nitranilines into the three nitrobenzonitriles (B. 28, 150; constitution, pp. 38, 105). The nitration of the benzonitrile yields m-nitrobenzonitrile almost exclusively. o-Nitrobenzonitrile has been obtained from o-nitraniline (B. 28, 151). Nitro-acids result upon saponifying the nitronitriles with caustic soda:

```
o-Nitrobenzoic Acid melts at 147°; o-Nitrobenzonitrile melts at 109°. m-Nitrobenzoic Acid ""141°; m-Nitrobenzonitrile ""116°. p-Nitrobenzoic Acid ""238°; p-Nitrobenzonitrile ""147°.
```

o-Nitrobenzoic Acid possesses a sweet taste and dissolves in 164 parts of water at 16°. Its nitration produces 2,6-, 2,5-, 2,4-dinitrobenzoic acids, and styphnic acid (p. 161). m Nitrobenzoic acid dissolves in 425 parts of water (160). Its barium salt dissolves with difficulty. Upon nitration it yields 2,5 dinitrobenzoic acid. p-Nitrobenzoic acid, called also nitrodracrylic acid, because it is formed in the action of nitric acid upon dragon's blood (p. 103) (A. 48, 344), is very sparingly soluble in water. Nitration converts it into 2.4 and 3.4-dinitrobenzoic acids. The electrolysis of its warm sulphuric acid solution produces p-amidophenolsulphonic acid (B. 28, R. 378; compare also B. 28, R. 126). 2,4-, 3,4-Dinitro- and 2,4,6-trinitrobenzoic acids are obtained by the oxidation of the corresponding nitroluenes (p. 68). The dinitrotoluenes are oxidized by chromic acid mixture (B. 27, 2209), or by potassium permanganate. Trinitrotoluene is oxidized by a nitric-sulphuric acid mixture at 150-2000.

2,4-Dinitrobenzoic Acid melts at 179°; the 2,5-acid melts at 177°; 2,6-acid at 202°; the 3.4-10id at 165°; the 3.5-, or ordinary dinitrobenzoic acid melts at 204°. 2.4.6-Trinitrobenzoic Acid, $(NO_2)_3C_6[I_1CO_2H]$, melts at 210° with the elimination of CO_2 (B. 27, 3154; 28, 2564, 3005; R. 125).

Nitro-haloid Benzoic Acids.—0,0 Fluornitrobenzoic Acid, C6H3F(NO2)COOH, melting at 127°, has been prepared by oxidizing fluornitrotoluene. In contrast with the other 0,0 disubstituted benzoic acids it can be quite readily esterified (see p. 197; B. 29, 842). The nitration of m-brombenzoic acid yields two o-nitro-acids, both of which yield anthranilic acid upon reduction: 3-brom-2-nitrobenzoic acid, melting at 250°, and 3 brom-6-nitrobenzoic acid, melting at 139° (compare equivalence of the six hydrogen atoms of benzene, p. 33). The halogen atom in the nitrohaloid benzoic acids is reactive, like that in the nitrohaloid benzenes (B. 22, 3282).

Nitrophenyl-acetic Acids, NO₂. C₆H₄. CH₂. CO₂H, are produced by saponifying the nitrobenzylcyanides with caustic alkali. The latter bodies constitute the product

resulting from the action of potassium cyanide upon the nitrobenzyl chlorides (p. 180),

(B. 16, 2064; 19, 2635). The nitration of phenyl-acetic acid produces mainly the paitro-body, with little of the o-nitro-acid and o,p-dinitrophenyl acetic acid, melting at 166°.

o-, m-, p-Nitrophenylacetic Acids melt at 141°, 120°, 152°. o-, m-, p-Nitrobenzyl Cyanides " 84°, 61°, 116°.

Nitrohydrocinnamic Acids, NO₂C₆H₄CH₂. CH₂. CO₂H.—p-Nitro- and o-nitrohydrocinnamic acids result from the nitration of hydrocinnamic acid. Both in turn yield the o,p-dinitro-acid. The o-nitro-acid is also prepared from o-nitro-p-amidohydrocinnamic acid, the first reduction-product of the o,p-dinitro-acid, as well as from o-nitrobenzyl-malonic ester (see this). The m-nitro-acid is obtained from p-acetamido-m-nitrohydrocinnamic acid (B. 15, 846; 29, 635; compare also m-nitrotoluene, p. 68).

o-, m-, p-Nitrohydrocinnamic Acids melt at 115°, 118°, 163°. o-p-Dinitrohydrocinnamic Acid melts at 123° (B. 13, 1680).

o- and p-Nitrohydratropic Acids, NO₄. C₆H₄. CH(CH₃). CO₅H, melting at 110° and 87°, are produced upon introducing hydratropic acid into strongly cooled, fuming nitric acid (A. 227, 262).

4. Nitrosomonocarboxylic Acids.—o-Nitrosobenzoic Acid, C₆H₄[1]NO[2]CO. - OH, melting with decomposition at 210°, results from the oxidation of the phenyl-

exyindols obtained from benzolnoxime (B. 29, 2064).

4. AROMATIC AMIDOMONOCARBOXYLIC ACIDS.

These are obtained by reducing the corresponding nitrobenzoic acids. Like glycocoll, the amidobenzoic acids yield crystalline salts both with acids and bases. They do not combine with acetic acid, hence are precipitated by it from their alkali salts.

Like glycocoll, these acids can be considered as cyclic ammonium salts (1, 354). The hydrogen atoms of the amido-group are replaceable by alkyl and acidyl residues. Dimethylated amido-acids are produced by the action of phosgene and aluminium chloride upon the dimethylanilines. Acetamidobenzoic acids are formed by the oxidation of the acetyl toluidines.

The o-amido-acids (of which o-amidobenzoic acid and o-amidophenylacetic acid are closely related to indigo, and o-amidohydrocinnamic acid to quinoline) form hetero-rings, and yield rather remarkable ortho-condensation products.

Anthranilic Acid, o - Amidobenzoic Acid, C₆H₄ { [1]CO₂H₁ or

C₃H₄ {[1]COO, melts at 145°, and breaks down, upon heating, into aniline [2]NH₂ and carbonic acid. Its aqueous solution has a sweet taste. It was first obtained from *indigo* (see this) by the action of caustic potash (Fritzsche, 1841). The oxidation can be accelerated by the addition of manganese dioxide (A. 234, 146). The acid results from the reduction of o-nitrobenzoic acid and the two m-brom-o-nitrobenzoic acids (p. 210) with tin and hydrochloric acid; also from phthalimide upon treatment with bromine and caustic potash (B. 24, R. 966), as well as from anthranil, acetanthranilic acid, and isatoic acid (see below).

Nitrous acid converts anthranilic acid in aqueous solution into sali-

cylic acid, and sodium in amyl alcohol solution into hexahydroanthranilic acid, hexahydrobenzoic acid (see this), and n-pimelic acid (1, 444) (B. 27, 2466).

The ethyl ether boils at 260°. It is formed when alcohol and hydrochloric acid act upon isatoic acid. Its amide, from isatoic acid and ammonia, melts at 108° (B. 18, R. 273). Phenylanthranilic acid, C₆H₆NH[2]C₆H₄[1]CO₂H, melts at 181° (B. 25, 1734) (below).

Formylanthranilic acid, CHO. NH[2]CaH4[1]CO2H, melting at 168°, is produced

in boiling isatoic acid with formic acid.

Acetylanthranilic Acid, CH₈CO. NH[2]C₈H₄[1]CO₂H, results when o-acetyltoluidine is oxidized, when o-amidobenzoic acid and anthranil are acted upon with acetic anhydride, and in the oxidation of methyl ketol and quinaldine with potassium permanganate. It melts at 185°. The ethyl ester, melting at 61°, and the amide, melting at 170°, are produced from the corresponding anthranilic acid derivatives by the action of acetic anhydride.

Benzoylanthranilic Acid melts at 183° (B. 26, 1304).

Anthranil, o-Amidobenzoic Acid Lactam, C₆H₄ {[1]CH or C₆H₆ {[1]N or C₆H₆

oil which volatilizes readily with aqueous vapor, possesses a peculiar odor, and boils with decomposition at about 210°. This inner anhydride of o-amidobenzoic acid has never been obtained from the acid itself, but (1) by the reduction of o-nitrobenzaldehyde with ferrous sulphate (theoretical quantity) and ammonia (B. 15, 2105, 2572), or with tin and glacial acetic acid (B. 16, 2227; 28, 1382). It also results (2) when o-nitrophenyloxy-acrylic acid is boiled with water (B. 16, 2222); anthroxanaldehyde is produced at the same time. It dissolves in alkalies, forming salts of anthranilic acid. o-Amidobenzaldehyde and o-amidobenzylalcohol are produced when it is reduced.

Methylcarboxyanthranilic Ester, CO₂H . NH[2]C₆H₄[1]CO₂CH₃, melting at 176°, is formed, together with anthranilic ester, when methyl alcohol at 130° acts upon isatoic

acid (B. 20, R. 813).

Carboxyethylanthranilamide, CO₂C₂H₅. NH[2]C₆H₄[1]CONH₂, melting at 152°,

results when ClCO₂C₂H₅ acts upon anthranilamide.

o. Uramidobenzoic Acid, NH2CONH[2]C₆H₄[1]CO₂H, melting at 152°, is formed in the interaction of the chlorhydrate of anthranilic acid and potassium cyanate.

Isatoic Acid, Anthranilcarbonic Acid, C₆H₄ [1]CO or C₆H₄ (CO.O) NH.CO.?), melts about 233-240°, decomposing at the same time into carbon dioxide and anthranil. It was first obtained by oxidizing a glacial acetic acid solution of indigo with chromic acid (II, Kolbe, 1885), and later from anthranil and anthranilic acid by the action of chlorcarbonic esters (B. 22, 1672). It is very sparingly soluble in water. Digested with alkalies or boiled with acids, it decomposes into carbon dioxide and anthranilic acid. Ammonia, hydrazine, phenylhydrazine, and hydroxylamine change it into the corresponding amide derivatives of anthranilic acid (B. 19, R. 65; 26, R. 585).

Kynuric Acid, Oxalylanthranilic Acid, Carbostyrilic Acid, CO₂H. CONH[2]C₄H₄. [1]CO₂H + H₂O, becomes anhydrous at 100° and melts at 180° with decomposition. It is formed from the quinoline derivatives—kynurine (see this), kynurenic acid (see this), a-phenylquinoline (see this), carbostyril (see this), acettetrahydroquinoline, and indoxylic acid (see this)—by oxidation. It is prepared synthetically by heating anthranilic acid with oxalic acid to 130° (B. 17, 401; R. 110). Its ethyl ester, CO₂. C₂H₅. CO. NH[2]C₆H₄[1]CO₂H₄, is formed in the oxidation of the ester of indoxylic acid (B. 15, 778). It melts at 180°.

Dicyanaminobenzoyl, C_6H_4 [1]CO. N

Dicyanaminobenzoyl, C_6H_4 [2]NH. C. CN, melts with decomposition. It results from cyanogen and o-amidobenzoic acid in aqueous solution (B. 11, 1986). Ethoxy-cyanaminobencoyl, C_6H_4 [1]CO. N

cyanaminobencoyl, C_6H_4 [2]NH. C. OC, H_5 , melting at 173°, is formed from cyanogen

and o-amidobenzoic acid in alcoholic solution (B. 2, 415). Ammonia changes it to o-benzglycocyamidine, benzoylenguanidine, C₈H₄ {[1]CO . NH which CH₈I in strong alkaline solution converts into a-o-benzcreatinine, C₈H₄ {[1]CO—NH {[1]CO—NH {[2]N(CH₉)—C: NH {[2]N(CH₉)—C: NH (B. 13, 977). Further derivatives of anthranilic acid have been obtained from 0 amidobenzonitrile, C₆H₄[1]NH₂[2]CN, melting at 47°; this results in the reduction of 0-nitronitrile (B. 29, 624).

Dibromanthranilic Acid is produced when bromine acts upon o-nitrotoluene (p. 68). Hetero-ring Formations of Anthranilic Acid and its Derivatives .- Anthranil and isatoic acid, whose constitution has not yet been definitely determined, are derivatives of anthranilic acid which certainly contain an hetero-ring, but both are not formed from anthranilic acid. However, numerous reactions of the latter acid lead to hetero-rings, which contain one, two, and three nitrogen atoms in the new ring (compare o-amidobenzylalcohol, p. 180; o-amidobenzylamine, p. 181; o-amidobenzaldehyde, p. 187, and o-amidoacetophenone, p. 190).

Acetylanthranilic acid and phenol condense on heating to acridone, which also results on digesting phenylanthranilic acid (p. 212) with concentrated sulphuric acid (B. 25, 2740). Anthranilic acid condenses with acetophenone and acetoacetic ester to quinoline derivatives (B. 27, 1396):

$$\begin{split} &C_{6}H_{4}\left\{ \begin{bmatrix} \mathbf{I} \end{bmatrix} CO_{9}H & -H_{5}O \\ \mathbf{2} \end{bmatrix} NHC_{6}H_{5} & -C_{9}H_{5}C_{9}H_{6}C_{0}NH \right\} C_{6}H_{4} & \text{Acridone} \\ &C_{6}H_{4}\left\{ \begin{bmatrix} \mathbf{I} \end{bmatrix} COOH & CH_{3} \cdot CO_{3} \cdot C_{3}H_{5} & -C_{3}H_{6}O \\ -HO_{3} & -HO_{3} \end{array} \right\} C_{6}H_{4} < \begin{matrix} C(OH) = C.CO_{3}H & \gamma \cdot Oxyquinal-dine \cdot \beta \cdot car-boxylic \cdot Acid \\ N & C.CH_{3} & \text{boxylic Acid} \end{matrix}$$

$$&C_{6}H_{4}\left\{ \begin{bmatrix} \mathbf{I} \end{bmatrix} COOH & CH_{3} & -2H_{2}O \\ 2]NH_{2} & + \begin{matrix} COH \\ CO.C_{6}H_{5} \end{matrix} \right\} & -2H_{2}O & -2H_{2}O \\ N & -2H_{2}O & \text{constant} \end{matrix}$$

$$C_6H_4\left\{ \begin{array}{l} \text{[1]COOH} \\ \text{[2]NH}_2 \end{array} \right. + \begin{array}{l} CH_3 \\ \text{CO.C}_6H_5 \end{array} \xrightarrow{-2H_2O} C_6H_4 < \begin{array}{l} C(\text{OH}) = CH \\ N : ---- C.C_6H_5 \end{array} \xrightarrow{\text{V-oxyquino}} C_5 C_6H_5 \end{array}$$

o-Benzoylenurea is formed on heating anthranilic acid and anthranilamide with urea. It also results upon heating carboxethyl-o-amidobenzamide (B. 2, 416; 22, R. 196), as well as by the action of mineral acids upon uramidobenzoic acid (B. 27, 976). Kétodi-Aydroquinasolines are produced on heating formyl-, acetyl-, and benzoyl-o-amidobenzamide. The β -methyl compound is formed in the action of acetamide upon anthranilic acid, and ammonia upon ethylacetamidobenzoic ester (B. 20, R. 630; 22, R. 196; 27, R. 516). The condensation products of o-amidobenzoic acid and cyanogen gas have been described and formulated (p. 212):

$$\begin{array}{c|c} C_0H_4\left\{ \begin{bmatrix} 1 \end{bmatrix} COOH & -H_7O \\ 2 \end{bmatrix} NH \cdot CO \cdot NH_2 & -C_2H_6O \\ \end{array} \right\} \\ \begin{array}{c|c} C_0H_4\left\{ \begin{bmatrix} 1 \end{bmatrix} CONH_2 & -C_2H_6O \\ 2 \end{bmatrix} NH \cdot COOC_2H_4 & -C_3H_6O \\ \end{array} \right\} \\ \begin{array}{c|c} C_0H_4\left\{ \begin{bmatrix} 1 \end{bmatrix} CO \cdot NH_2 & -H_2O \\ -H_4CO & -H_4CO \\ \end{array} \right\} \\ \begin{array}{c|c} CO \cdot NH & \delta \cdot Keto \cdot dihydroquinazoline. \\ \end{array}$$

Nitrous acid converts anthranilamide directly into benzazimide, whereas the o-diazo-this change (B. 21, 1538; R. 571):

$$\begin{cases} [1]CONH_{\bullet} & NOOH \\ [2]NH_{\bullet} \cdot HCI & NO$$

m- and p-Amidobenzoic Acids melt at 173° and at 186°.

Chrysanisic Acid, 3,5 Dinitro-4-amidobenzoic acid, (NO₂)₂(NH₂). C₂H₂CO₂H, melting at 259°, consists of golden yellow leaflets, and is produced when 3,5-dinitro-4-

methoxybenzoic acid is heated with aqueous ammonia.

Diamidobenzoic Acids, (NH₂)₂C₄H₃CO₂H, are prepared by reducing the dinitroand the nitroamidobenzoic acids. They break down in dry distillation into carbon dioxide and phenylenediamines (p. 94). Like the o-phenylenediamines (p. 95), the diamidobenzoic acids, containing two amido-groups in the ortho-position with reference to each other, readily yield hetero-cyclic derivatives—e. g., nitrous acid converts 34-diamidobenzoic acid into 3,4-acimidobenzoic acid (B. 15, 1880) (p. 96). The m.p. and the p.m-amidouramidobenzoic acids yield two different uramidoazimidobenzoic acids, which afford the same azimidobenzoic acid by saponification (B. 29, R. 586).

which afford the same azimidobenzoic acid by saponification (B. 29, R. 586). 3,4,5-Triamidobenzoic Acid, (NH₂)₃. C₆H₂. CO₂H, from chrysanisic acid by reduction, breaks down, when heated, into CO₂ and 1,2,3-triamidobenzene (A. 163, 12).

2,3,5-Triamidobenzoic Acid (B. 15, 2199).

Many amido-acids, derived from alkyl-benzoic acids, are known; also haloid amido-

acids, nitro-amido-acids, etc.

Amidophenyl-fatty Acids are obtained from the nitrophenyl-fatty acids. Certain o-amidophenyl-fatty acids are particularly noteworthy because of their tendency to form inner anhydrides: γ - or δ -lactams (1, 359), which is so great that the corresponding free o-amido-acids are not capable of existing—e. g., o-amidophenyl-acetic acid and o-amidophenylhydrocinnamic acid.

m- and p-Amidophenyl-acetic Acids melt at 149° and 200°.

m- and p-Amidohydrocinnamic Acids " 84° " 131°.

4-Amido-3-nitrohydrocinnamic Acid, from p-acetamidohydrocinnamic acid, melts at 145°.

p. Amidohydratropic Acid, melting at 128°, is converted into phloretic acid (A. 227

267) by nitrous acid.

y- and δ -Lactams of the o-Amidophenyl-fatty Acids.—Anthranil can be regarded as the simplest o-amido-acid lactam. However, its constitution has not been satisfactorily established, and it has not been obtained from anthranilic acid. The next higher homologues are:

Oxindol, the lactam of o-Amidophenyl-acetic Acid, C_6H_4 $\left\{ \begin{bmatrix} 1\\2 \end{bmatrix} CH_3 \cdot CO \\ NH_{--}I \right\}$, melting at 120°, is obtained by the reduction of o-nitrophenyl-acetic acid with tin and hydrochloric acid, and from dioxindol with sodium amalgam. If heated to 150° with barytawater it is converted into the barium salt of o-amidophenyl-acetic acid, from which oxindol is separated by acids (B. 16, 1704). Nitrous acid converts it into isatoxime (see this).

(see this).

Oxindol boiled with acetic anhydride yields Aceto-oxindol, C₆H₆ {[1]CH₂.CO melting at 126°. It dissolves to aceto-o-amidophenyl-acetic acid, CH₂.CO.NH.C₆H₄.CH₂.CO₂H, melting at 142°. Heated with alkalies or acids it breaks down into oxindol and acetic acid.

p-Amido-oxindol, NII₂. C₈H₆NO, melting about 200°, is formed by the reduction of 2,4-dinitrophenyl-acetic acid (p. 211) with tin and hydrochloric acid. If ammonium sulphide be used as the reducing agent, the product will be 4-Amido-2-nitrophenyl-acetic acid, melting at 185° (B. 14, 824); compare o-nitrophenylisonitroso-acetic acid.

Atroxindol, lactam of o-amidohydratropic acid, C₆H₄ { [1] CH(CH₈) . CO, melts at

Πο°.

Hydrocarbostyril, lactam of Amidohydrocinnamic Acid, melting at 163°, is formed by the reduction of o-nitrohydrocinnamic acid with tin and hydrochloric acid (Glaser and Buchanan, 1869) (B. 15, 2103), and by heating hydrocarbostyril-carboxylic acid, result-

ing from the reduction of o-nitrobenzylmalonic acid (B. 29, 667). Hydrocarbostyril sustains the same relation to quinoline that oxindol bears to indol:

$$C_{6}H_{4}^{\left[1\right]CH_{2},CH_{3}}, Hydrocarbostyril; C_{6}H_{4}^{\left[1\right]CH} = CH_{1}, Quinoline.$$

p-Amidohydrocarbostyril, NH₂C₃H₃NO, melting at 211°, is formed, together with 4-amido-2-nitrohydrocinnamic acid, melting at 139°, from 2,4-dinitrohydrocinnamic acid.

5. Diazobenzoic Acids (p. 98) are produced from the mineral acid salts of the amidobenzoic acids with nitrous acid, just as the ordinary diazo-bodies are obtained from the control of the same acid acid with nitrous acid, just as the ordinary diazo-bodies are obtained from the aniline salts. Nitrous acid converts the amide of o-amidobenzoic acid into benzaz-imide (p. 213). Nitrates of the three diazobenzoic acids are produced from the nitrates of the three amidobenzoic acids. They explode violently on the application of heat. The perbromides of the three diazobenzoic acids are also known. When the nitrates are boiled with water they yield oxybenzoic acids; the sulphates are converted by haloid acids into haloid benzoic acids (B. 18, 960). The free diazobenzoic acids are very unstable. The diaxide of anthranilic acid, C_6H_4 $\left\{ \begin{bmatrix} 1\\2 \end{bmatrix}N_2 > 0 \right\}$, consists of white, glistening needles. It is obtained when the chloride is acted upon with silver oxide (B. 29, 1535).

6. Diazoamidobenzoic Acids (p. 106) are formed when nitrous acid is conducted into the alcoholic solution of the amidobenzoic acids. Diazo-m-amidobenzoic Acid. $CO_2H[1]C_6H_4[3]N = N - NH[3']C_6H_4[1']CO_2H$, is an orange-red powder. Hy-

drofluoric acid converts it into m-fluorbenzoic acid (p. 114):

$$\begin{array}{l} \text{CO}_2\text{H[1]C}_6\text{H}_4\text{[3]N} \\ \text{CO}_2\text{H[1]C}_6\text{H}_4\text{[3]NH} \end{array}) N + 2\text{HFI} = \frac{\text{CO}_2\text{H[1]C}_6\text{H}_4\text{[3]FI}}{\text{CO}_2\text{H[1]C}_6\text{H}_4\text{[3]NN}_2\text{HFI}} + N_2. \end{array}$$

7. Diazoimidobenzoic Acids, N/N. C₆H₄CO₂H (p. 110), result upon letting am-

monia act upon the perbromides of diazobenzoic acids, or when hydrazine-benzoic acids are treated with nitrous acid. The o-body melts about 70°; the meta at 160°, and the p-compound at 185° (B. 9, 1658).

N. C₆H₄CO₂H 8. Azoxybenzoic Acids, O < N. C₆H₄CO₂H, are formed in the reduction of the nitrobenzoic acids with alcoholic potash (p. 111). The o-derivative is also produced when n-oxyindolcarboxylic acid (see this) is oxidized with alkaline potassium permanganate (B. 17, 1904; 24, R. 666; 29, 656).

9. Azobenzoic Acids, i N. C₆H₄. CO₂H The action of sodium amalgam upon the

mononitrobenzoic acids produces these acids.

Azobensene-p-monocarboxylic acid has been obtained from amidoazobenzene (B. 19, 3022). o., m., and p-Azobenzoic acids are decomposed on fusion. Azophenylene or phenazine is formed when the calcium salts are distilled.

10. Hydrazine-benzoic Acids.—The symmetrical hydrazobenzoic acids result when the azobenzoic acids are reduced with sodium amalgam, or with ferrous sulphate and sodium hydroxide. o-Hydrazobenzoic Acid melts at 205°. m-Hydrazobenzoic Acid, CO₂H[3]C₆H₄[1]NH.NH[1']C₆H₄[3']CO₂H. These two acids, when boiled with hydrochloric acid, rearrange themselves to diamidodiphenyldicarboxylic acids (see these). The rearrangement of the m-acid into p-diamidodiphenic acid is of importance for the proof of the constitution of diphenic acid (see this), and consequently that of phenanthrene.

o-, m-, and p-Hydrazine-benzoic Acids, NH2. NH. CaH4. CO2H, re-

sult when the hydrochlorides or nitrates of diazobenzoic acids are re-Thionyl aniline converts them into o-, m-, and p-bensoic-acid thionyl hydrazones, melting at 155°, 231°, and 258° (B. 27, 2555).

o-Hydrazine-benzoic acid, when heated, changes to a lactum of o-

hydrazine-benzoic acid, CeH4 { [1]CO NH, melting at 242° with decomposition (A. 212, 333).

 Sulphobenzoic Acids.—On conducting the vapors of SO₂ into benzoic acid, we obtain as chief product m-Sulphobenzoic Acid, and in smaller amount p-Sulphobenzoic Acid (A. 178, 279).

The three isomerides can be obtained by oxidizing the three toluene sulphonic acids

with an alkaline solution of potassium permanganate (p. 192).

If the toluene sulphamides, instead of the free acids, be subjected to similar oxidation, the m- and p-toluene sulphamides yield m- and p-sulphamine-benzoic acids; whereas the o toluene sulphamide changes to benzoic sulphinide, or anhydrosulphamine-benzoic acid, called saccharin (B. 12, 469). Hydrochloric acid reconverts this at 150° into o-sulphobenzoic acid.

o-Sulphobenzoic Acid when anhydrous melts at 250°. In deportment it recalls phthalic acid (see this). It forms, for example, phthaleins, an anhydride and an imide. PCls produces two dichlorides, melting at 22° and 76°, which probably have the formulas C6II4 COCI and C6II4 CCl2>O (B. 29, R. 355). o-Sulphobenzoic Anhydridi, $C_6H_4\left\{\begin{bmatrix} 1\\ 2\end{bmatrix}SO_2\right\}$ O, melting at 118°, is obtained from the acid by the action of acetyl chloride. The *nitrile*, o-cyanbenzene-sulphonic acid, $C_6H_4(CN)SO_2H$, is obtained from the diagram compound (B. 28. R. 751).

the o-aniline sulphonic acid (p. 137) through the diazo-compound (B. 28, R. 751). o-Sulphamine benzeic Acid, SO₂NH, [2]C₂H, [1]CO₂H, melts at 153-155°, changing at the same time into the sulphinide. It is produced by oxidizing o-toluene sulphamide with potassium ferricyanide (B. 19, R. 689), and from its inner anhydride by digesting with caustic soda. Isomeric o-Benzamide-sulphonic acid, C6H4(CONH2)SO2H (B. 29, R. 102), is formed when sulphobenzoic acid is fused with ammonium sulphocyanide

(B. 29, R. 102).

- o-Anhydrosulphamine-benzoic Acid, Benzoic Sulphinide, $C_8H_4\begin{bmatrix}1\\2\end{bmatrix}SO_2$ NH, called saccharin, melts at 220°. It was discovered in 1879 by Ira Remsen and C. Fahlberg. Its preparation was given above. This compound is now made technically in very large quantities. It is used for sweetening purposes. It is 500 times sweeter than cane-sugar. It dissolves with difficulty in cold water, and, like succinimide and phthalimide, behaves like a strong acid, forming imide-salts. The sodium salt, $C_6H_4\left\{egin{bmatrix}1\ 2\end{bmatrix}SO_2>NNa$, is very readily soluble in water, and is 400 times sweeter than cane-sugar. It is readily transposed by such haloid derivatives as benzyl chloride and acetyl chloride to N-derivatives of saccharin (B. 25, 1737; 29, 1048).
- o-Sulphobenzoic-anil, $C_6 II_4 \left\{ \frac{SO_2}{CO} > N \cdot C_6 II_5$, melting at 190°, results from the action of aniline upon the chlorides of sulphobenzoic acid (B. 29, R. 353). Phosphorus pentachloride converts saccharin into pseudosaccharin-chloride, C₈H₄ [1]CCl N, melting at 149° (B. 29, 2995).

All sulpho-acids containing the sulpho-group in the o-position with reference to the carboxyl group of an alkylbenzoic acid are capable of forming sulphinides or sulpho-

carbonimides (B. 25, 1737).

3,5-Disulphobenzoic Acid is produced by sulphonating benzoic acid with H.SO, and P.O. (B. 27, R. 118). 2,4-Disulphobenzoic Acid is obtained from 2,4-toluene-disulphonic acid (B. 14, 1205).

(1 b). MONOHYDRIC OXYPHENYL-PARAFFIN ALCOHOLS AND THEIR OXIDATION PRODUCTS.

E. MONOHYDRIC OXYPHENYL-PARAFFIN ALCOHOLS, OR PHENOL ALCOHOLS.

These alcohols contain, in addition to the alcoholic hydroxyl, other hydroxyl groups joined to the benzene nucleus, which impart to them the character of phenols. Some of the alcohols of this group are simple transposition products of long-known plant substances.

Formation.—Some of the methods described under the benzyl alcohols

also lead to phenol alcohols:

The reduction of corresponding aldehydes and ketones.
 The treatment of aldehydes with caustic alkali.

(3) The action of sodium amalgam upon amides (B. 24, 175).

(4) They are linked to the benzyl alcohols through the amidophenylparaffin alcohols, which nitrous acid converts into oxyphenyl-paraffin alcohols.

(5) Nucleus-synthesis: Methylene chlorides (B. 13, 435) or formaldehyde and sodium hydroxide (B. 27, 2411; J. pr. Ch. [2] 50, 225) change

phenols into phenyl alcohols.

Monoxybenzyl Alcohols, HOC₄H₄. CH₂OH.—The three theoretically possible isomerides have been prepared. They result when the corresponding aldehydes are reduced with sodium amalgam. Saligenin, or o-Oxybenzyl alcohol, is the best-known member of the group:

Saligenin, or o-Oxybenzyl Alcohol, was first obtained in the decomposition of the glucoside salicin (see this) by means of emulsin, ptyaline, or dilute acids (Piria, 1845; A. 56, 37):

$$C_6H_{11}O_6$$
. O. C_6H_4 . CH_9 . OH + $H_9O = HO \cdot C_6H_4$. CH_9 . OH + $C_6H_{12}O_6$ Salicin Glucose.

Saligenin has also been prepared by the common methods from salicylaldehyde, salicylamide, o-amidobenzyl alcohol, and phenol. It is soluble in hot water, alcohol, and ether. Ferric chloride produces a deep blue color in its solutions. Acids resinify it, forming saliretin (ρητίνη, Ethers and substitution products of saligenin are known. have been made in part from the corresponding salicyl-derivatives.

o-Oxybenzylamine, Salicylamine, melts at 121° (B. 23, 2744).

p-Oxyphenylethylamine, see tyrosine (see this).

Anisyl Alcohol, p-Methoxybenzyl Alcohol, CH₃O[4]C₆H₄[1]. CH₂. OH, is obtained from anisic aldehyde by alcoholic potassium hydroxide. It melts at 45° and boils at 259°. It forms anisic aldehyde when oxidized.

p-Homosaligenin, CH₂[5]C₂H₂[2](OH)CH₃. OH, melts at 105°.

Hydrocumarone, C₄H₄ { [1]CH₃. CH₂, boiling at 188°, is the inner anhydride of ooxyphenyl-ethyl alcohol, not known in the free state. It is formed when sodium in alco-11-19

hol acts upon cumarone (B. 25, 2409). p. Thymotin Alcohol, CII3[2]C3H1[5]C6H1[4].

()H[1]CH, OH, melts at 120° (B. 27, 2412).

Dioxybenzyl Alcohols are not known in a free condition, but derivatives of 2,5-dioxy- and of 3,4-dioxybenzyl alcohol have been obtained in the reduction of certain aldehyde-ethers with sodium amalgam. Dimethyl-gentisin Alcohol, (CH₂O)₂[2,5]C₂- H₃[1]CH₄. OH, boils at 278°.

l'anilly! Alcohol, CH3O[3]HO[4]C8H3[1]CH2. OH, from vanillin, melts at 115°.

Piperonyl Alcohol, CH₃<0[3] C₆H₃[1]CH₂. OH, from piperonal, melts at 51°. o Dioxybenzylamine melts at 168° (B. 27, 1799).

2. AROMATIC OXYMON-ALDEHYDES, PHENOL ALDEHYDES.

The phenol aldehydes are obtained (1) by oxidizing the phenol alcohols with chromic acid; (2) by an important nucleus-synthetic method, consisting in letting chloroform and an alkaline hydroxide act upon phenols (reaction of Reimer) when the chloroform enters the o- and p-position with reference to the phenol hydroxyl, and is then converted into the aldehyde group (B. 9, 1268):

$$C_6H_5$$
. OH + CHCl₃ + 4KOH = $C_6H_6 < \frac{OK}{CHO} + 3KCl + 3H_9O$.

Behavior.—All the phenol aldehydes show the same reactions of the aldehyde group as the benzaldehydes. Oxidizing agents convert them with difficulty into oxyacids; this is most easily accomplished by fusion with caustic alkalies. They reduce an ammoniacal silver solution, but not the Fehling solution. They dissolve in alkalies, forming salts— ϵ . g., $C_6H_4(CHO)$. ONa; the alkyl iodides convert the latter into alkyl ethers.

a. Monoxybenzaldehydes, HO. C₆H₄. CHO.—Three are possible according to theory; all of them are known. Anisic aldehyde, the methyl ether of p-oxybenzaldehyde, has been known for the longest

period.

Salicylic Aldehyde, o-Oxybenzaldehyde, formerly called salicylous or spiroylous acid, boils at 196°. Its sp. gravity equals 1.172 (15°). It occurs in the volatile oils of the different varieties of Spiraa—e. g., Spiraa ulmaria. It is obtained by the oxidation of saligenin and salicin (Piria, 1839) and by the decomposition of helicin, an oxidation product of salicin (see this). It is most readily prepared (together with p-oxybenzaldehyde) by the action of chloroform and caustic potash upon phenol. It is separated from the p-body by distillation in steam, in which salicylic aldehyde is very volatile. It is rather easily soluble in water; the solution is colored a deep violet by ferric chloride (compare saligenin, p. 217, and salicylic acid, p. 222). Like all ortho-oxyaldehydes, it colors the skin an intense yellow. Sodium amalgam transforms it into saligenin; oxidizing agents change it to salicylic acid.

Potassium salicylic aldehyde, C₆H₄(OK)CHO + H₂O, consists of yellow plates. The methyl ether, C₆H₄(O. CH₃). CHO, melts at 35° and boils at 238°; the ethyl ether boils at 248°. The acet-derivative, CH₃. CO. O. C₆H₄. CHO, melts at 37° and boils at 253°. Glucose derivative, see Helicin. o-Aldehydophenoxy-acetic acid, CO₂H. CH₂O-[2]C₆H₄[1]CHO, melting at 132°, splits off water and becomes coumarilic acid (see this). Salicyl aldoxime melts at 57°; comp. B. 22, 3320. o-Anisaldoxime, CH₂O. [2]C₆H₄-

[1]CH: N(OH), melts at 92° (B. 23, 2741). The phenylhydrazone melts at 142° (B.

Consult B. 22, 2339, upon the nitrosalicylaldehydes.

m-Oxybenzaldehyde results in the reduction of m-oxybenzoic acid with sodium amalgam (B. 14, 969) and from m-nitrobenzaldehyde (B. 15, 2045). It melts at 104° and boils at 240°. Its oxime melts at 87°. Its hydrazone melts at 130° (B. 24, 826). Its nitration produces three mononitro-compounds. See B. 18, 2572, for the nitro-mmethoxybenzaldehydes.

p-Oxybenzaldehyde is formed from phenol, chloroform, and caustic alkali, together with salicylic aldehyde. It melts at 116°, and sublimes. Its aldoxime melts at 65°; its hydrazone at 178°. Consult B. 29, 2302, 2355, for the haloid p-oxybenzaldehydes. Its methyl ether, readily accessible, is the so-called—

Anisic Aldehyde, p-Methoxybenzaldehyde, CH₃O[4]C₆H₄[1]-CHO, boiling at 248°, with sp. gr. 1.123 (15°). It results in oxidizing anethol (see this), present in various essential oils (anise, fennel, etc.), with dilute nitric acid or a chromic acid mixture.

Homologous Monoxybenzaldehydes have been prepared from various phenols by Reimer's method (p. 218). Thus:

o-Cresol gave	o-Homosalicylic Aldehyde, o-Homo-p-oxybenzaldehyde,	M. P. 17° 115°	B. P. 208° (B. 24, 3667).
m-Cresol "	m-Homosalicylic Aldehyde, m-Homo-p-oxybenzaldehyde,		222°.
p-Cresol "	p Homosalicylic Aldehyde,	56°	217°.
Thymol "	[3,5,6]-Trimethyl Salicylic Aldehyde, p-Thymotin Aldehyde,	133°	(B. 18, 2656). (B. 16, 2097).
Carvacrol, " p-Isobutylphenol "	p-Carvacrotin Aldehyde, p-Isobutyl Salicylic Aldehyde,	liquid "	(B. 19, 14). 252° (B. 28, R. 468).

The o-oxybenzaldehydes are more readily soluble in water and more sparingly soluble in chloroform than the p-oxybenzaldehydes. The o-bodies are volatile in steam, form sparingly soluble sodium bisulphite derivatives, and are colored yellow by ammonia (B. 11, 770); compare coumarines.

b. Dioxybenzaldehydes.—Some of the dioxybenzaldehydes which have been prepared by the chloroform-potash reaction are ethereal derivatives of protocatechuic aldehyde, and are characterized by an agreeable odor. This is especially true of vanillin and piperonal, or heliotropine. Both substances are prepared on a technical scale:

$$C_8H_3$$

$$\begin{cases} [1]CHO \\ [3]OH \\ [4]OH \end{cases}$$

$$C_8H_8$$

$$\begin{cases} [1]CHO \\ [3]OCH_8 \\ [4]OH \end{cases}$$

$$C_8H_3$$

$$\begin{cases} [1]CHO \\ [3]O \\ [4]O \end{cases}$$

$$C_8H_3$$

$$\begin{cases} [1]CHO \\ [3]O \\ [4]O \end{cases}$$

$$C_1OH_2$$

$$C_2OH_3$$

$$C_3OH_3$$

$$C_3$$

Protocatechuic Aldehyde, 3,4-Dioxybenzaldehyde, melting at 153° (B. 26, R. 701), was first obtained from piperonal (Fittig and Remsen, 1871); also from vanillin, isovanillin, and opianic acid with dilute hydrochloric acid. It is prepared in the nucleus-synthetic way from pyrocatechin by the chloroform reaction. It dissolves readily in water. Ferric chloride colors its aqueous solution a deep green (p. 159). It reduces ammoniacal silver solutions. Molten caustic potash converts protocatechuic aldehyde into protocatechuic acid. Its phenylhydrazone exists in two modifications: a- (stable), melting at 176°, and β- (unstable), melting at 121-128°. Its oxime melts at 150° (B. 29, R. 670).

Vanillin, m-Methoxy-p-oxybenzaldehyde, melting at 80°, sublimes readily, and is the active constituent of the vanilla bean pod (Vanilla

planifola), which contains about two per cent. (B. 9, 1287) of it. Vanillin also occurs in the orchid Nigritella suaveolens (B. 27, 3049). It was first prepared artificially from the glucoside coniferine (see this) by its oxidation with chromic acid (Tiemann and Haarmann, 1874; B. 7, 613). Glycovanillin (see this) was obtained as an intermediate product in the oxidation of coniferine; acids or emulsin split it up into glucoses and vanillin (B. 18, 1595, 1657). Vanillin is also produced by oxidizing eugenol (see this) (B. 9, 273). In the nucleus-synthetic way it has also been formed, together with m-methoxyl-salicylic aldehyde, boiling at 266°, from guaiacol, chloroform, and caustic potash (B. 14, 2023).

Heated with HCl it decomposes into CH₂Cl and protocatechnic aldehyde. It behaves like a p-oxybenzaldehyde, and protocatechuic acid results on fusion with potassium hydroxide—two facts from which its constitution may be concluded. Nascent hydrogen converts vanillin into vanillyl alcohol, hydrovanilloin, corresponding to hydrobensoln.

Vanillin-oxime melts at 117° (B. 24, 3654).

Trithiovanillin, [C₆H₃(OH)(OCH₂)CSH]3, melts at 236° (B. 29, 143).

Isovanillin, p-Methoxy-m-oxybenzaldehyde, melting at 116°, smells, when heated, like

vanilla and anise oil. It is obtained by oxidizing hesperitinic acid or by heating opianic acid with hydrochloric acid.

Dimethylprotocatechnic Aldehyde, CaHa(O. CHa), CHO, melts at about 42° and boils near 283° (B. 11, 662).

Piperonal, Protocatechuic Aldehyde-methylene Ether, Heliotropine, (CH,O,)CH, CHO, melting at 37° and boiling at 263°, was obtained by the oxidation of pipere acid (see this). It is also formed by treating protocatechuic aldehyde with alkali and methylene iodide. Its odor is pleasant, like that of heliotrope. Piperonylic acid results from its oxidation and piperonyl alcohol from its reduction (p. 218). Its oxime melts at 110°. Its phenythydrazone melts at 100°. PCl₅ converts it into piperonal chloride, (CH₂O₃) Coll₃CHCl₃, and dichlorpiperonal chloride, (CCl₃O₃). C₆H₃CHCl₂, which is changed by cold water into dichlorpiperonal, (CCl₂O₃). C₆H₃CHO, and with warm water it yields CO₂, HCl and protocatechuic aldehyde (A. 159, 144; B. 26, R. 701). Brompiperonal, (CH₂O₃). C₆H₂Br. CHO (B. 24, 2592). o-Nitro-piperonal yields bidioxymethylene indigo (B. 24, 617). The following bodies have been prepared from resorcinol and hydroquinone by the action of chloroform and caustic alkali, just as protocatechuic aldehyde was made from pyrocatechin.

β-Resorcyl aldchyde, (HO)₂[2,4]C₆H₂[1]CHO, melts at 135°.

Gentisin-aldchyde, (HO)₂[2,5]C₆H₃[1]CHO, melts at 99°.

Dioxyaldehydes are also produced in dilute solutions when much chloroform and caustic potash are used. The monomethyl ethers of resorcinol and hydroquinone, like guaiacol, each yield, upon treatment with chloroform and potash, two aldehydes—one, comparable in deportment with salicylaldehyde, contains the aldehyde group in the o-position with reference to phenol hydroxyl; while the other contains the aldehyde group in the pposition, referred to the free phenol hydroxyl (B. 14, 2024).

c. Tri- and Tetraoxybenzaldehydes.—Alkyl ethers of these bodies have been formed by oxidizing aromatic plant derivatives, containing unsaturated aliphatic side-

chains (B. 16, 2112; 17, 1086; 24, 3818).

Glycosyringaldehyde, an oxidation product of syringine (see this), when treated with emulsin yields a trioxybenzaldehyde ether (B. 22, R. 107).

3. PHENOL KETONES.

They have been obtained (1) from amidoketones (B. 18, 2691) and (2) from aromatic β -ketone-carboxylic acids (B. 25, 1308). The nucleus-synthetic methods, consisting in the introduction of acid radicals into phenols and phenol ethers, are better adapted for

the purpose; (3) the condensation of phenols with glacial acetic acid and other fatty acids by zinc chloride or tin tetrachloride (B. 14, 1566; 23, R. 43; 24, R. 770); better still, by phosphorus oxychloride (B. 27, 1983); (4) from phenols by means of acid chlorides (B. 22, R. 746); (5) from phenol alkyl ethers and acid chlorides in the presence of aluminium chloride (B. 23, 1199).

o-Oxyacetophenone, boiling at 213°, is formed by method 2. p-Oxyacetophenone, melting at 107°, is produced by method 1. p-Acetylanisol, p-methoxyacetophenone, melting at 38° and boiling at 258°, is formed by method 3. Propionylphenol, HOC₆II₄-COCH melting at 18° in readuced by method 4.

COC₂H₃, melting at 148°, is produced by method 4.

Acetopyrocatechol, (HO)₁[3,4]C₆H₃[1]CO. CH₄, melts at 116° (B. 27, 1989). Acetonillon, HO[4](CH₃O)[3]C₆H₃[1]COCH₃, melting at 115°, is produced in the oxidation of aceteugenol, and synthetically from guaiacol by method 5 (B. 24, 2855, 2869).

2123). Its p-methyl ether-

Pseconol, CH₂O[4](HO)[2]C₂H₃. CO. CH₃, melting at 45°, occurs in the root-bark of *Paonia Moutan*, a ranunculus from Japan (B. 25, 1292). When resorcinol diethyl ether is acetylated with the aid of aluminium chloride the products are 1,2,4-Resaceto-

phenone Diethyl Ether, melting at 69°, and an isomeric resacetophenone with the melting point 178° (B. 29, R. 386). Consult B. 29, R. 674, for haloid resacetophenones.

Quina-acetophenone, (HO)₂[2,5]C₆H₃[1]CO. CH₃, melting at 202°, is produced by method 2. Valerohydroquinone, (HO)₂[2,5]C₆H₃. CO. C₄H₉, melts at 115°. Its quinhydrone results when sunlight acts upon benzoquinone and valeric aldehyde (B. 24,

Gall-acetophenone (HO), [2,3,4]C, H, [1]CO. CH, melting at 168°, is formed by method 3 (B. 27, 2737).

4. PHENOL MONOCARBOXYLIC ACIDS.

The aromatic oxy-acids containing hydroxyl united to the benzene nucleus combine the character of acids and phenols, hence are designated Should the hydroxyl groups enter the aliphatic sidephenol acids. chains, we would obtain aromatic alcohol acids, showing in their deportment very great similarity to the oxy-fatty acids.

Formation.—A. From substituted carboxylic acids, as in the case of the phenols: (1) Through the conversion of the amido-acids, by means of nitrous acid, into diazo-compounds and then boiling the latter with water. (2) By fusing the sulphobenzoic acids with alkalies. The haloid benzene carboxylic acids react like the sulpho-acids when subjected to similar treatment.

B. From compounds in which the phenol hydroxyl is always present. (3) By fusing homologous phenols with alkalies, when the methyl group, linked to the nucleus, will be oxidized to the carboxyl group. (4) By oxidizing the sulphuric or phosphoric acid esters of homologous phenols and then saponifying the resulting phenol-carboxylic esters. (5) By fusing the phenol aldehydes, difficult to oxidize, with alkalies. (6) By converting the phenol aldoximes into oxy-acid nitriles and then saponifying the latter.

Nucleus-synthesis: (7) By the action of carbon dioxide upon the dry sodium salts of the phenols at elevated temperatures, when the carbonic acid generally enters the ortho-position with reference to the hydroxyl group. This reaction will be more exhaustively discussed in connection with salicylic acid.

(8) By boiling the phenols with carbon tetrachloride (1, 387) and caustic

potash (B. 10, 2185):

$$C_6H_5$$
. OH + CCl_4 + 5KOH = $C_6H_6 < \frac{OH}{CO_6K}$ + 4KCl + 3H₂O.

This reaction is perfectly analogous to that of the formation of oxyal-dehydes by means of chloroform and caustic alkali. As a general thing the carboxyl group enters the para-position with reference to phenol hydroxyl. o-Oxy-acids are produced in smaller amounts.

(9) When urea chloride, phenylisocyanate, and phenyl mustard oil, together with aluminium chloride, act upon phenol ethers (or thiophenol ethers) in carbon disalphide solution (A. 244, 61; B. 27, 1733), the products are amides, anilides, and thio anilides of alkyl oxy-acids.

Behavior.—They are monobasic acids. The hydrogen of the carboxyl group is alone

replaced by metals when they are acted upon with alkaline carbonates.

Their hydroxyl hydrogen can also be replaced by alkalies, forming basic salts—e.g., CoNa Carbon dioxide, however, will convert the latter into neutral salts. The ether esters manifest a like deportment, inasmuch as it is only the alkyl ester which is eliminated, with the production of a salt of an alkyl-ether acid:

$$C_6H_4 < CO_2 \cdot CH_3 + KOH = C_6H_4 < CO_2K + CH_3 \cdot OH.$$

The o-oxy-acids, unlike the m- and p-derivatives, volatilize in aqueous vapor, are colored violet by ferric chloride, and dissolve in chloroform. The m-oxy-acids are colored red-dish-brown when heated with concentrated sulphuric acid, with the formation of oxyathraquinones (B. 18, 21.42). They are usually more stable than the o- and p-acids. Boiling concentrated hydrochloric acid decomposes the p-acids into carbon dioxide and phenols. All the oxy-acids decompose into carbon dioxide and phenols when distilled with lime.

A. Monoxy-mono-carboxylic Acids.—Salicylic acid or o-oxybenzoic acid is by far the most important representative of this class. It is extensively applied both in therapeutics and in the color industry.

Monoxybenzoic Acids.—The three isomerides theoretically pos-

sible are known.

Salicylic Acid, o-Oxybenzoic Acid, HO[2]C₆H₄[1]CO₂H, melting at 155°, occurs in a free condition in the buds of *Spiraa ulmaria*, as the methyl ester in oil of *Gaultheria procumbens* (oil of wintergreen), a species of Ericaceæ. It is produced, by the general methods of formation, (1) from anthranilic acid; (2) from o-sulpho-, o-chlor-, and o-brombenzoic acids; (3) from o-cresol; (4) from saligenin and salicylal-dehyde; (5) from phenolates with CO₂; and (6) with carbon tetrachloride.

It is also formed upon fusing coumarin (see this) and indigo (see this) with caustic potash, and in the distillation of copper benzoate.

Technical Preparation.—Two methods of bringing sodium phenolate and CO₂ in reac-

tion are applicable for this purpose:

(a) Sodium phenoxide is heated in a current of carbon dioxide at 180-220°, when the

latter is absorbed. Half of the phenol distils over, and the residue consists of disodium salicylate (H. Kolbe):

$$2C_6H_6$$
. ONa + $CO_3 = C_6H_4 < \frac{ONa}{CO_4Na} + C_6H_5$. OH.

The behavior of potassium phenolate in this reaction is remarkable. At 150° dipotassium salicylate is produced. At a more elevated temperature, however, there is formed with the dipotassium salicylate its isomeride, dipotassium paraoxybenzoate. latter is more abundant in proportion to the increased temperature, until at 220° it is the sole product. The primary alkali salicylates, when heated, show the following deportment:

Monosodium salicylate at 220° yields disodium salicylate, phenol, and CO₂:

$${}_{2}C_{6}H_{4} \underbrace{\overset{CO_{3}Na}{OH}}_{OH} = C_{6}H_{4} \underbrace{\overset{CO_{3}Na}{ONa}}_{ONa} + C_{6}H_{6}OH + CO_{3}.$$

Primary potassium salicylate at 220° yields phenol, dipotassium paraoxybenzoate, and

CO. Primary sodium paraoxybenzoate at 280° yields phenol, CO₃, and disodium salicylate

(J. pr. Ch. [2] 16, 425).

(b) Sodium phenoxide is saturated under pressure, in closed vessels, with carbon dioxide, when it is converted into sodium phenocarbonate, C_6H_6 . O. CO₂Na. By continuing the pressure and applying a heat of 120–130°, this salt is changed to sodium salicylate: $HO[2]C_6H_6[1]CO_3Na$. The second method shows a complete transformation of the phenol.

History.—Piria first obtained salicylic acid in 1838, when he oxidized its aldehyde with molten caustic potash (A. 30, 165). In 1843 Cahours proved that wintergreen oil consisted almost entirely of methyl salicylic ester (A. 53, 332). Gerland in 1853 showed that anthranilic acid, as suspected by A. W. Hofmann, could be converted by nitrous acid into salicylic acid (A. 86, 147). In 1860 H. Kolbe and Lautemann prepared it synthetically from phenol, sodium, and carbonic acid (A. 115, 201). It was Kolbe who first correctly interpreted salicylic acid to be a monobasic oxyacid, and in 1874 discovered that the acid could readily be formed upon conducting carbon and in 1874 discovered that the acid could readily be formed upon conducting carbon dioxide over dry and heated sodium phenate. It was in this way that he ascertained the conditions serving for the production of the acid upon a technical scale. R. Schmidt discovered the conversion of sodium phenocarbonate under pressure at 120-130° into monosodium salicylate (B. 17, R. 624).

Properties and Behavior.—Salicylic acid crystallizes from alcohol in colorless prisms; from hot water in long needles. It has a sweet, acid taste. It dissolves in 400 parts of water at 15°, and in 12 parts at 100°; it is very soluble in chloroform. When it is heated alone, salol, or phenylsalicylic ester, and xanthone (see this) are produced (A. 269, 323). Sodium in amyl alcohol solution reduces it to normal pimelic acid. In this reaction the ring is ruptured and ketohexamethylene carboxylic acid appears as an intermediate product (B. 27, 331).

Its aqueous solution acquires a violet coloration upon the addition of ferric chloride. It is a powerful antiseptic, arrests decay and fermentation (Kolbe, J. pr. Ch. [2] 10, 9), and is applied therapeutically both as the free acid and in the form of its sodium salt (in rheumatism of the

Salicylates.—Sodium Salicylate, HO. $C_8H_4CO_2Na$, is a crystalline powder with an unpleasant sweet taste. Basic Calcium Salicylate, $(OC_8H_4CO_2)Ca + H_2O$, dissolves with great difficulty, and is precipitated upon boiling salicylic acid with lime-water. It serves for the separation of salicylic acid from m- and p-oxybenzoic acids.

Esters, Ethers, and Ether Esters.—Methyl Ester, HO. C.H. CO. CH., boiling at 224°, with sp. gr. 1.197 (0°), is the chief ingredient of wintergreen oil (from Gaultheria procumbens). It occurs in many different plants in the form of a glucoside (B. 29, R. 511).

When the methyl ester is digested with an alcoholic solution of potassium hydroxide and methyl iodide, we get the dimethyl ester, C₈H₄. CO₂. CH₃, boiling at 245°. Boiled with potassium hydroxide it is saponified, yielding methyl alcohol and methyl salicylic acid, C₆H₄CO_.CH₃, melting at 98°. It decomposes into carbon dioxide and anisol when heated to 200°.

Phenol Salicylic Ester, Salol, HO. CaH₄. CO₂. CaH₅, melting at 43° and boiling at 172° (12 mm.), results on heating salicylic acid alone to 200–220°, with the eliminating salicylic acid alone to 200–220°, which alone to 200–20°, which alone nation of water and carbon dioxide; from salicylic acid, phenol, and POCla; from polysalicylide on heating with phenol, or when phosgene acts upon the sodium salts of salicylic acid and phenol. It is applied as an antiseptic. It changes to xanthone (see this), or diphenylene ketone oxide, when it is heated. When sodium salol, C₆H₄(ONs) CO₂. C₂II₅ (from salol and sodium), is heated to 280-300°, it changes to the isomeric sodium salt of *phenylsalicylic acid*, C₆H₄(O. C₆H₅). CO₂H, which melts at 113°, and is not colored by ferric chloride.

Thiosalol, IIO. C₆H₄COSC₆H₅, melting at 54°, results upon heating salicylic acid and thiophenol with PCl₃ or POCl₃. Phenylthiosalicylic Acid, C₆H₅SC₆H₄CO₃H, melts at 166° (A. 263, 2). See Thioxanthone.

Aceto-salicylic Acid, CH₃CO.O.C₆H₄.CO₂H, melts at 118°.

Salicyl Chloride, HO.C₆H₄COCl, is not known. It is true that PCl₅ acts very energetically upon salicylic acid, but the resulting phosphoroxychloride is transposed by the phenol hydroxyl, with evolution of hydrochloric acid:

$$C_6H_4\Big\{{\tiny\begin{bmatrix}1\]COOH_PCI_6\\2\]OH}\xrightarrow{PCI_6}C_6H_4\Big\{{\tiny\begin{bmatrix}1\]COCI_POCI_9\\2\]OH}\xrightarrow{PCI_6}C_6H_4\Big\{{\tiny\begin{bmatrix}1\]COCI_POCI_9\\2\]OPOCI_9}\Big\}$$

and there results:

o-Chlorcarbonylphenyl-orthophosphoric acid dichloride, melting at 168° (II mm.). If the PCl, continues to act, this compound will exchange an oxygen atom for two chlorine atoms, and o Trichlormethylphenyl-orthophosphoric acid dichloride, (Cl.PO)O[2]C.H. [1]CCl., boiling at 178° (11 mm.) will be formed. When this is heated with PCl. in a sealed tube to 180°, there results:

o-Chlorbenzotrichloride, Cl[2]CaH4[1]CCla, melting at 30° and boiling at 130° (II mm.) (A. 239, 314). m- and p-Oxybenzoic acids, as well as m- and p-cresotinic acids, behave similarly.

If, however, the hydrogen atom of the phenol hydroxyl is replaced by the methyl or

acetyl group, then PCl₅ produces the chlorides:

Methyl Salicyl Chloride, CH₃O[2]C₆H₄[1]COCl, boiling at 254°, and Acetyl Salicyl Chloride, CH₃CO₂[2]C₆H₄[1]COCl, melting at 43° and boiling at 135° (12 mm.).

When halogen atoms, nitro groups, or methyl groups are introduced into salicylic acid, and then occupy the o-position with reference to the phenol hydroxyl, the latter will be and then occupy the o-position with reference to the phosphorus oxychloride. Consequently, in the action of PCl_b free oxychlorides will be produced:

o-Cresotinic Chloride, HO[2]C₆H₃[3]CH₃[1]COCl, melting at 28°; 3-Chlorsalicyl Chloride, melting at 63°; [3,5]-Dichlorsalicyl Chloride, melting at 79°, and [3,5]-Dichlorsalicyl Chloride, melting at 70° (B. 30, 221).

The influence of substituents in the vicinity of the phenol hydroxyl group is manifested in other ways, as in that of the esterification of [2,6] substituted benzoic acids with

slicohol and hydrochloric acid (p. 197).

Salicylo-phosphorous Chloride, $C_6H_4\left\{\begin{bmatrix}1\\2\end{bmatrix}\right\}O$ —>PCl, melting at 30° and boiling at 167° (11 mm.), is readily formed when PCl₂ acts upon salicylic acid at 70° (A. 239, 301). All substituted salicylic acids react similarly (B. 30, 221).

 $O.C_6H_4.COO.C_6H_4.CO$

Salicylide or Tetrasalicylide, CO. C₆H₄. CO. C₆H₄. CO. C₆H₄. CO. C₆H₄O. Salicylide, (C₇H₄O₃)x, melting at 322-325°, are produced when POCl₃ acts upon salicylic acid in xylene solution. The two compounds are separated by means of boiling chloroform, with which the tetrasalicylide forms a compound, Salicylide Chloroform, (C₁H₆O₂)₄. 2CHCl₂, crystallizing in beautiful quadratic octahedra, which contain 33 per cent. of chloroform loosely combined as chloroform of crystallization. This body has been used technically in the preparation of pure chloroform (Anschütz, A. 273, 94). o-Cresotinic acid and the o-haloid salicylic acids behave similarly.

Salicylamide, HO. CaH4. CONH2, melts at 138° (B. 24, 138). Salicylanilide, CaH4(OH)CONHCaH5, changes, when heated in dry condition, to acridone, $C_{H} <_{NH}^{CO} > C_{H}$ It is very probable that it is at first rearranged into phenyl anthranilic acid (p. 213) (B. 29, 1189). Salicylo-nitrile, HO. C₄H₄. CN, melting at 98°, is obtained from salicylaldoxime and acetic anhydride (B. 26, 2621; 27, R. 134).

Substituted Salicylic Acids.—The 5-derivatives of the mono-substitution products are

the most readily prepared. 3-Derivatives are formed simultaneously. Of the disubstituted salicylic acids the 3,5-derivatives are made with the most ease. In them the substituents sancync acids the 3,5-derivatives are made with the most ease. In them the substituents enter the op-position, referred to phenolhydroxyl. 5-Chlor-, 5-brom-, 5-iod-, and 5-nitro-alicylic acids melt at 172°, 164°, 196°, and 228°. 3-Chlor-, 3-brom-, 3-iod-, and 3-nitrosalicylic acids melt at 178°, 220°, 193°, and 125°. 3,5-Dichlor-, 3,5-dibrom-, 3,5-diiod-, and 3,5-dinitrosalicylic acids melt at 214°, 223°, 220°–230° with decomposition, and at 173°. An anhydride, melting at 187° (B. 30, 223), has been prepared by the action of the chloride of 3,5-dichlorsalicylic acid upon the silver salt.

m-Oxybenzoic Acid, HO[1]C₆H₄[1]CO₂H, melts at 200° and sublimes without decomposition. p-Oxybenzoic Acid, HO[4]C₆H₄[1]CO₂H, melts when anhydrous at 210° with partial decomposition into carbon dioxide and phenol. Its method select males at

with partial decomposition into carbon dioxide and phenol. Its methyl ester melts at 131° and boils at 270-280° (B. 27, R. 570). The two acids are obtained from their corresponding amido- and haloid benzoic acids by methods I and 2 (p. 221). See p. 223 for the production of p-oxybenzoic acid, together with salicylic acid, by methods 7 and 8. p-Oxybenzoic acid is also obtained from many resins by fusing them with caustic potash. For the behavior of m- and p-oxybenzoic acids with PCl, consult p. 224. Compare A. 261, 236, for the action of chlorine upon the three oxylenzoic acids.

Anisic Acid, p-Methoxybenzoic Acid, CH3O[4]C6H4[1]CO2H, melting at 185° and boiling at 280°, is like benzoic and salicylic acids, one of the acids which has been long known. It is isomeric with methyl salicylic ester, and the other monomethyl derivatives of the oxybenzoic acids in general, as well as with the oxyphenylacetic acids. Anisic acid is easily obtained, hence numerous transposition-products of it are known. It is prepared by oxidizing anethol, the chief ingredient of anise oil, and other ethercal oils containing anethol (see this), with dilute nitric acid or with a chromic acid mixture.

History.—Cahours (1839) discovered anisic acid when he oxidized anise oil (A. 41, 66). Kolbe at first considered it methoxybenzoic acid, because when it was distilled with caustic baryta it broke down into CO₂ and anisol (p. 146). Saytzew (1863) found that when anisic acid was heated with hydriodic acid it yielded an acid different from salicylic acid, yet isomeric with the latter (A. 127, 129). This was subsequently found to be p-oxybenzoic acid. In 1867 Ladenburg showed that anisic acid could be prepared by saponifying the dimethyl ether-ester of p-oxyhenzoic acid (A. 141, 241).

Oxytoluic Acids or Cresotinic Acids, CH₃, C₆H₃(OH). CO₂H.—The ten possible isomerides are known (B. 16, 1966). They are isomeric with the three oxyphenylacetic acids (p. 226), the three oxymethylbenzoic acids or benzyl alcohol carboxylic acids, and phenyl glycollic acid or mandelic acid. They have been prepared from the toluic acids by methods 1 and 2, from the oxyaldehydes by method 5, and from the cresols by methods

7 and 8 (p. 222).

3-, 4-, 5-, and 6-Methylhomosalicylic Acids melt at 163°, 177°, 151°, and 168°. 2., 4., 5., and 6 Methylhomo-m oxybenzoic Acids melt at 1830, 2060, 2080, and 1720. 2- and 3-Methylhomo-p-oxybenzoic Acids melt at 177° and 172°.

Those isomerides containing the hydroxyl-group in the ortho-position with reference to carboxyl, are colored violet by ferric chloride, just like salicylic acid. They dissolve easily in cold chloroform and are volatile with steam. See p. 224 for their behavior toward PCl₅, PCl₅, PCl₅, etc. 3. Methylhomosalicylic acid yields an o-homosalicylide- or o-cresolide-chloroform (A. 273, 88) similar to salicylide-chloroform. 5. Methyl-m-oxybenzoic acid, prepared synthetically by the action of barytn-water moon acetone oxalic ester (B. 22, 3271), yields by nitration nitrococcic acid or 2,4,6-trinitrein o.y m-toluic acid, melting at 180°, which is also formed when carminic acid (see this), the dye of red cochineal, is oxidized (B. 26, 2648). When the three isomeric cresolinic acids, or, better, their dibrom-substitution products are reduced with sodium and anyl alcohol, the ring is ruptured and a_1 , β_2 , and γ_2 -methylpimelic acids are produced (A. 295, 173; compare p. 47).

o- and p-Oxymesitylenic Acids, HO. CaH, (CH,), CO, H, melt at 179° and 223°

(A. 206, 197).

Di- and tri-methyloxybenzoic acids (B. 21, 884), as well as ethylmethyloxybenzoic acids (A. 195, 284), are also known. The corresponding isopropyloxybenzoic acids— Thymo- and iso-oxycumic acids, melting at 142° and 94° (B. 19, 3307)—result upon fusing carvacrol and thymol (p. 144) with caustic potash.

Different isomeric p-methylisopropyloxybenzoic acids, (CH₃)(C₃H₇)C₄H₂(OH)COOH: thymotic and carvacrotinic acids have been made by introducing the CO, group into thymol and carvacrol. See B. 28, 2795 for the derivatives of thymotic acid.

The oxyphenyl-fatty acids attach themselves to the alkyl-substituted oxybenzoic acids. They are produced (I) by diazotizing the corresponding amidophenyl-fatty acids and then decomposing the diazo-derivatives with boiling water; (2) by saponifying the oxybensyl cyanides.

The o-oxyacids, in which the phenol hydroxyl-group occupies the y- or b-position with reference to the carboxyl-group, are, in contrast to the corresponding oamido fatty acids (p. 214), capable of existing, but when heated they part with water and

yield y and d-lactones (1, 334, 345, 346).

The exphenylacetic acids, 11(), C₆H₄, CH₂, CO₂H, are isomeric with the ten oxytoluc acids (see these), with the three oxymethylbenzoic acids, and with the mandelic acids. o Oxyphenylacetic acid, bearing close relationship to oxindol (p. 214) and isatin (see this), is also obtained from o oxymandelic acid by reduction with hydriodic acid. Ferric chloride colors it violet. It passes into its lactone (see below) when it is heated. p-Oxythenylacetic Acid occurs in urine, and arises from the decomposition of albuminous hoolies as well as in that of sinalbin, occurring in the seeds of white mustard (B. 22, 2137).

o, m., and p. Oxyphenylacetic Acids melt at 137°, 129°, and 148°. m. and p. Oxy-

thenylacetonitrile melt at 52° and 69° (B. 22, 2139).

Oxyphenylpropionic Acids.—Four of the six theoretically possible acids are known.

Phloretic Acid, p-Oxyhydratropic Acid, HO[4]C₆H₄[1]CH<CO₉H, melting at 129°, is formed, together with phloroglucin, when phloretine (the phloroglucin ester of phloretic acid) is digested with potassium hydroxide. It has been prepared synthetically from p-amidohydrocinnamic acid (p. 214). Ferric chloride colors its solution green. Baryta decomposes it into ethyl phenol; fusion with potassium hydroxide produces paraoxybenzoic acid.

Phloretine, Monophloreticphloroglucin Ester, $(HO)_2C_6H_2O \cdot CO \cdot CH(CH_2) \cdot -$ Coll (1) II, melts at 2540 (B. 27, 1631, 2686). See phlorisine.

Hydrocoumaric Acids, or 3-Phenolpropionic Acids, HO. C. H. CH. CH. $C(O_2)$ 11, result when the corresponding coumaric acids, the oxycinnamic acids, or β -oxyphenylacrylic acids are reduced with sodium amalgam.

o Hydrocoumaric Acid, or Melilotic Acid, melting at 81°, occurs free and in combination with coumarin, the lactone of o-oxycinnamic acid, in the yellow melilot (Melilotus officinalis). It is produced by the action of sodium amalgam upon coumarin. Ferric chloride imparts a bluish color to the solution. When distilled, it passes into its lactone—hydrocoumarin. It yields salicylic acid when it is fused with caustic potash.

m- and p-Hydrocoumaric Acids melt at III° and I28°. p-Hydrocoumaric acid is

also produced in the decay of tyrosine.

 γ - and δ -Lactones of δ -oxyphenyl-fatty acids are produced when these acids are distilled. They correspond to the γ - and δ -lactams described on p. 214.

o-Oxyphenylacetic Acid Lactone, C₈H₄ { [1]CH₃ · CO, melts at 49° and boils at 236° (B. 17, 975).

Hydrocoumarin, β -o-Oxyphenylpropionic Acid Lactone, C_6II_4 $\left\{\begin{bmatrix} 1\\2\\0 \end{bmatrix}$, melts at 25° and boils at 272°. When boiled with water it regenerates the acid from which it was produced by distillation.

B. Dioxymonocarboxylic Acids are obtained by the same methods which were used in the preparation of the aromatic monocarboxylic acids. The carboxyl group is more readily introduced into the dioxybenzenes than into the monoxybenzenes. This occurs upon heating the bodies with a solution of ammonium or sodium carbonate to 100° or 130° (B. 18, 3202; 19, 2318). The dioxybenzoic acids break down, when heated, into carbon dioxide and dioxybenzenes.

Dioxybenzoic Acids.—The six possible isomerides are known.

The most important member of this class is—

Protocatechuic Acid, 3,4-Dioxybenzoic Acid, (HO)₁[3,4]C₆H₃[1]CO₂H + H₂O, melts when anhydrous at 190°, and decomposes into pyrocatechin and carbonic acid. It occurs in the fruit of *Illicium religiosum*. It has been obtained from many triderivatives of benzene, containing substituents in the 3,4-position with reference to a side-chain, by fusing them with caustic potash—e. g., from the corresponding bromand iod-p-oxybenzoic acids, bromanisic acid, p- and m-cresolsulphonic acid; sulpho-p-, and sulpho-m-oxybenzoic acids, from eugenol, piperic acid (compare also piperonylic acid, p. 228), etc., as well as from various resins (benzoīn, asaſœtida, myrrh, and particularly kino) on fusion with potassium or sodium hydroxide. The latter resin readily yields large quantities of the acid (A. 177, 188). Compare further phloroglucin ethers of protocatechuic acid. It is also produced by the action of bromine upon quinic acid in aqueous solution.

The two possible pyrocatechuic monocarboxylic acids are produced when pyrocatechin is heated to 140° with a solution of ammonium car-

bonate.

Ferric chloride colors the solution green; after the addition of a very dilute soda solution it becomes blue, later red (all derivatives containing the protocatechuic residue, (OH)₂C₆H₃.C—B. 14, 958, react similarly). Ferrous salts color its salt solutions violet. It reduces an ammoniacal silver solution, but not an alkaline copper solution. Diprotocatechuic Acid, C₁₆H₁₀O₇, is a tannic acid which results on boiling protocatechuic acid with aqueous arsenic acid. It is very similar to common tannic acid, but is colored green by ferric oxide. It forms a compound with p-oxybenzoic acid by the union of equimolecular quantities (A. 134, 276; 280, 18).

See naphthalene ring formations for the conversion of substituted protocatechuic acids,

by oxidation with nitric acid, into derivatives of β -naphthoquinone.

The phenol ethers of protocatechuic acid are:

$$\begin{array}{c} C_6H_3 \left\{ \begin{bmatrix} 1 \end{bmatrix} CO_2H \\ \begin{bmatrix} 3 \end{bmatrix} OCH_3 \\ \begin{bmatrix} 4 \end{bmatrix} OH \\ \end{bmatrix} C_6H_3 \left\{ \begin{bmatrix} 1 \end{bmatrix} CO_2H \\ \begin{bmatrix} 4 \end{bmatrix} OCH_3 \\ \end{bmatrix} C_6H_3 \left\{ \begin{bmatrix} 1 \end{bmatrix} CO_2H \\ \begin{bmatrix} 3 \end{bmatrix} OCH_2 \\ \end{bmatrix} C_6H_3 \left\{ \begin{bmatrix} 1 \end{bmatrix} CO_2H \\ \end{bmatrix} C_6H_3 C_4H_3 C_4$$

These alkyl- and alkylen-ether acids are formed when protocatechuic acid is treated with CH₂I, CH₂I, and CH₂Br. CH₄Br and caustic potash, as well as by oxidizing the corresponding ethers of protocatechuic aldehyde. The protocatechuic acid can be regained from them upon heating with hydrochloric acid to 150°, when the dimethyl ether acid will yield at first the two monomethyl ether acids; whereas the methylene ether, piperonylic acid, separates carbon in addition to protocatechnic acid:

$$CO_2H \cdot C_6H_3 < {}^{\raisebox{-0.5ex}{O}} > CH_2 = CO_2H \cdot C_6H_3 < {}^{\raisebox{-0.5ex}{O}} + C.$$

The alkyl ether-acids break down into carbon dioxide and alkyl pyrocatechnic ethers

when they are heated with lime or baryta.

Vanillic Acid, m-Methylprotocatechnic Acid, melting at 211°, sublimes. It is obtained by the energetic oxidation of its aldehyde, vanillin (p. 219), also from coniferine, as well as by the decomposition of acetvanillic acid, melting at 142°, the oxidation product of acetesgenol, acetferulic acid, and acethomovanillic acid, when they are treated with potassion permanganate. Its nitrile melts at 87° (B. 24, 3654).

Isovanillic Acid, p. Methylprotocatechuic Acid, melts at 2500, and was first obtained from hemipinic acid (see this), or 4,5-dimethoxy-o-phthalic acid upon heating with hydro-

Veratric Acid, 3,4-Dimethoxybenzoic Acid, melting at 179.5°, occurs, together with veratrin (see the alkaloids), in the sabadilla seeds (from Veratrum Sabadilla).

Diethyiprotocatechnic acid melts at 149°.

Piperonylic Acid, Methylene-protocatechuic acid, melting at 228°, is also formed by oxidizing a homopiperonylic acid, obtained from safrol, as well as from piperonal and protocatechnic acid (see this). It breaks down when heated with hydrochloric acid (see above). Its nitrile melts at 95° (B. 24, 3656).

Ethylene protocatechuic acid melts at 133°

The phloroglucin ethers of protocatechnic acid are probably certain vegetable substances which, upon fusion with caustic potash, break down into phloroglucin (p. 165) and protocatechnic acid. They are:

Luteolin, $C_{13}H_{10}O_6$ (B. 29, R. 647, 848), occurs in *Reseda luteola* and crystallizes in yellow needles. Ferric chloride colors it green.

Catechin, $C_{13}H_{13}O_6$ (?), from catechu, and Maclurin or Moringa Tannic Acid, C₁₃H₁₀O₆ · H₂O, from yellow wood, *Morus tinctoria*, are generally included among the tannic acids. *Proteaic Acid*, C₂H₁₀O₄, appears to be a homologue of protocatechuic acid. It is present in *Protea mellifera* (B. 29, R. 415).

Pyrocatechin-o-carboxylic Acid, 2,3-Dioxybenzoic Acid, (HO)₂C₆H₂CO₂H + 2H₂O,

melts at 199° when anhydrous. It readily breaks down into CO, and pyrocatechin, from which it is formed, together with protocatechuic acid, by the action of ammonium carbonate (A. 220, 116). It also results when 3-iodsalicylic acid is fused with caustic potash.

Resorcinol Monocarboxylic Acids.—There are three. Sym.-dioxybenzoic acid results on heating sym. disulphobenzoic acid (p. 216) with caustic potash, and the other two acids are produced when resorcinol is treated with ammonium dicarbonate or potas-

sium dicarbonate solution (B. 18, 1985; 13, 2379)

The a-compound is not colored by ferric chloride; whereas the β -body is colored a dark red and the) modification blue-violet by the same reagent.

a-Resorcylic Acid, 3,5-Dioxybenzoic Acid, (HO), C6H3CO3H + 1 1/2H2O, melts at 233°. It yields anthrachrysone (see this), when it is heated with sulphuric acid.

B. Resorvylic Acid, 2,4-Dioxybenzoic Acid + 3H2O, melts in the anhydrous state at

213°. See B. 28, R. 1051; 29, R. 30, for the ethers and esters of the acid.

It is converted in glacial acetic acid solution by chlorine into hexachlor m-diketo-Rhexene (B. 25, 2687). The nitrile melts at 175°.

y-Reservelic Acid, 2,6-Dioxybenzoic acid, melts at 148-167° and breaks down into

CO, and resorcinol.

Gentisinic Acid, Hydroquinone Carboxylic Acid, 2,5-Dioxybenzoic Acid, melts at 200°, and at 215° breaks down into carbon dioxide and hydroquinone. It was first prepared from gentisin (see this), a xanthone derivative, together with phloroglucin, on ing it with caustic potash. It is obtained from 5-brom-, 5-iod-, and 5-amidosalicylic acids; also from hydroquinone and from gentisinic aldehyde (B. 14, 1988). Ferric

chloride colors it a deep blue and is decomposed into CO₂ and quinone (B. 18, 3499).

The Dioxytoluic Acids, (HO)₂C₆H₂(CH₃)CO₂H, are isomeric with the dioxyphenylectic acids. The most important of the known acids of this class is Orsellinic Acid, 2.6-dioxy-p-toluic acid, which melts at 176° and breaks down into CO₂ and orcinol (p. 162). It is obtained from orsellic acid upon boiling the latter with water, or erythrin

with baryta-water. It is colored violet by ferric chloride.

Orsellic Acid, diorsellinic acid or lecanoric acid, $C_{16}H_{14}O_{17}$, melting at 153°, is an ether-like anhydride of orsellinic acid, $(HO)_2 \cdot C_9H_2(CH_3) \cdot CO \cdot OC_6H_2(OH)(CH_3) \cdot CO_9H$ (?). It is found in different mosses of the varieties Roccella and Lecanora. Boil-

Oph (r). It is found in unitation and in the line water converts it into orsellinic acid.

Erythrin, C₂₉H₂₂O₁₀ + 1½H₂O, Erythrinic Acid, is an ether-derivative of di-orsellinic acid and erythrite. It occurs in the lichen Roccella fuciformis, which is applied in the lichen Roccella fuciformis, which is applied in the lichen Roccella fuciformis. When it is boiled with water it breaks up into orsellinic acid and-

Picro-erythrin, C₁₂H₁₆O₇ + H₂O, which, boiled with baryta-water, yields erythrite,

orcin, and carbon dioxide:

Erythrin
$$C_{30}H_{20}O_{10} + H_2O = (HO)_2C_6H_2(CH_2)CO_3H + C_{12}H_{16}O_7$$
 Picro-erythrin $C_{12}H_{16}O_7 + H_2O = (HO)_2C_6H_3CH_3 + CO_2 + C_4H_6(OH)_4$ Erythrol.

Everninic Acid, $C_3H_{10}O_4 = (HO)_3C_6H(CH_3)_2CO_2H(?)$, is produced, together with ossellinic acid, on boiling evernic acid (from Evernia prunastris) with baryta. It

melts at 157°, and is colored violet by ferric chloride.

Dioxydurylic Acid, pseudocumene hydroquinone carboxylic acid, (HO),[2,5]C6-[3,4,6](CH₃)₂CO₃H, melts at 210° when rapidly heated, and results from the reduction of Durylic Acid Quinone, pseudocumene quinone carboxylic acid, O₄[2.5]C₆[3,4,6]. (CH₃₎₂CO₃H, which decomposes at 130°, and is obtained by the action of ferric chloride apon a hydrochloric acid solution of diamidodurylic acid (A. 237, 11).

Dioxyphenyl-fatty Acids.—Certain dioxyphenylacetic acids and dioxyphenylpropi-

onic acids in this group are interesting.

a-Homoprotocatechuic Acid and its ether-acids have their side-groups occupying the same positions as those of protocatechuic acid and its ether-acids:

$$\begin{array}{c} C_{6}H_{3} \begin{pmatrix} CH_{3} \cdot CO_{2}H & (1) \\ OH & (3) \\ OH & (4) \end{pmatrix} \\ \text{e-Homoprotocatechulc Acid,} \\ \text{m. p. } 142^{\circ} \end{pmatrix} \begin{array}{c} C_{6}H_{3} \begin{pmatrix} CH_{3} \cdot CO_{2}H & (1) \\ O \cdot CH_{3} & (3) \\ OH & (4) \\ \text{e-Homoprotopic porolytic Acid,} \\ \text{m. p. } 142^{\circ} \end{pmatrix} \\ \text{e-Homopropic porolytic Acid,} \\ \text{m. p. } 127^{\circ} \\ \end{array}$$

The acet- α -homovanillic acid and α -homopiperonylic acid result in the moderated oxidation of aceteugenol (see this) and safrol (see this) with KMnO4. The former melts at 140° and is converted by caustic soda into a-homovanillic acid, which hydrochloric acid, at 180°, changes to a-homoprotocatechuic acid (B. 10, 207; 24, 2882).

Symmetrical Dioxyphenyl-acetic Acid, (HO), [3,5]C, H, [1]CH, CO, H + H,O,

melts at 54°.

The triethyl ester, obtained from the dicarboxylic acid derived from this acid, is produced by the condensation of acetone dicarboxylic ester with sodium. It melts at 98° and yields dioxyphenyl-acetic acid upon saponification. It yields orcin when its silver salt is heated.

Hydrocaffele Acid, or β -3,4-dioxyphenylpropionic acid, corresponds, like a-homoprotocatechnic acid, with the same arrangement of the substituting groups as in protocatechnic acid, to-

{{1}сн₂ сн₂.со₂н [1]CH2.CH2.CO2H ([1]CH₂ CH₂ CO₂H (i)ch*ch*co^ti Сен { Ізюсн (3lon (slo. Сана { [3]ОСНа [4]0 (14)OCH [4]OCH₂ [4]OH Hydrocaffeic Dimethyl Ether Acid, m. p. 960 Hydroisoferulic Acid, m. p. 164° Hydrocaffeic Methylene Ether Acid, m. p. &c. Hydroferulic Acid, m. p. 890

Hydrocaffele acid itself and its ether-acids are formed from the corresponding [3,4]. dioxycinnamic or cassel and their derivatives, serulic and isoserulic acids, by reduction with sodium amalgam (B. 11, 550; 13, 758). The methylene ether-acid is also produced by oxidizing β-hydropiperic acid (see this) (B. 20, 421). Ferric chloride colors hydrocassel acid the same as it does protocatechuic acid (p. 227).

Hydro-umbellic Acid, β-2,4-dioxyphenylpropionic acid. (HO)₂[2,4]C₂H₂. CH₄. CH₄. CO₂H₃ decomposes at 110°. It is obtained from umbelliseron, the δ-lactone of

[2,4] dioxycinnamic acid, by the action of sodium amalgam. Ferric chloride colors

it green.

Trioxybenzoic acids, (HO)₂C₆H₂CO₂H. Three of the six possible isomerides are known. The most important is—

Gallic Acid, (HO), [3,4,5]C₆H₂CO₂H + H₂O. It melts and decomposes about 220° into CO₂ and pyrogallol. It occurs free in tea, in the fruit of Ciesalpina coriaria (Divi-divi), in mangoes, and in various other It is obtained from the ordinary tannic acid (tannin) by boiling it with dilute acids. It is prepared artificially from brom-s-m-dioxybenzoic acid and brom-protocatechuic acid when fused with potassium hydroxide.

Gallic acid crystallizes in fine, silky needles. It dissolves with difficulty in cold water, but readily in hot water, alcohol, and ether. It has a faintly acid, astringent taste. It reduces both gold and silver salts (hence its application in photography). Ferric chloride throws down a

blackish-blue precipitate in its solutions.

The solutions of its alkali salts absorb oxygen when exposed to the air, and, in consequence, become brown in color.

Rufigallic Acid, a derivative of anthracene (see this), is obtained by heating gallic

acid with sulphuric acid.

Oxidizing agents, such as arsenic acid and iodine, convert gallic into Ellagic Acid,

probably a fluorene derivative.

In alkaline solution gallic acid is converted into galloflavin (see this), a yellow dye of the xanthone group. Hydrochloric acid and potassium chlorate decompose the acid into isotrichlorglyceric acid or trichlorpyroracemic acid (II, 45).

Basic Bismuth Gallate, (110)3C6H2CO2Bi(OH)2, under the name dermatol, is applied

as an odorless drying antiseptic.

Ethyl Gallic Ester, (HO)₃C₆H₂CO₂C₂H₅, melts at 141°, when anhydrous. Trimethyl and triethyl gallic ether-acids, (R'O)₃C₆H₂CO₂H, melt at 168° and 112°. Methylene methyl gallic ether-acid, myristicinic acid, (CH₃O)(CH₄O₂). C₆H₂CO₂H, melts at 130-135° (B. 24, 3821) when it is anhydrous. Triacetyl Gallic Acid melts with decomposition at 170°. Gallic Acid Anilide, Gallanol, has been used in medicine. This is true also of dibromgallic acid, or gallobromol, melting at 140°.

Pyrogallol-carboxylic Acid, $(H(1))_3[2,3,4]$ -C₆H₂CO₂H + $\frac{1}{2}$ H₂O₄ is prepared by heating pyrogallol with potassium bicarbonate (B. 18, 3205). It decomposes a 195-200°, but sublimes without decomposition in a current of carbon dioxide. Femi chloride colors it violet. Triethyl-pyrogallol-carboxylic Acid, C6H2(O.C3H5)3. CO1H

melts at 105°. It results in the oxidation of triethyldaphnetic acid (see this).

Phloroglucin Carboxylic Acid, (HO)_s[2,4,6]C_sH₂CO₂H + H₂O, decompose even at 100°, also when boiled with water, into carbon dioxide and phloroglucin, from which it is obtained by boiling with a potassium carbonate solution (B. 18, 1323).

Triethyloxyhydroquinone Ether-acid, $(C_2H_5O)_3[2,4,5]C_6H_3CO_3H$, melting at 134°, results upon treating a- or β -sesculetine triethyl ether-acid with potassium permanganate (B. 16, 2113).

Asaronic Acid and Syringaic Acid (p. 220) are methyl ether-acids, derived from tri-

oxybenzolc acids.

Iridic Acid, a-homodimethyl gallic ether-acid, (CH₃O)₃(HO)[3,4,5]C₆H₃CH₃CO₂H, melting at 118°, is produced along with formic acid and iretol when irigenine is decomposed with baryta-water (B. 26, 2015).

Addendum: Tannic Acids.—The tannins or tannic acids are substances widely disseminated in the vegetable kingdom. They are soluble in water, possess an acid, astringent taste, are colored dark blue or green (ink) by ferrous salts, precipitate gelatine, and enter into combination (leather) with animal hides (gelatine). Hence they are employed in the manufacture of leather, and for the preparation of ink. They are precipitated from their aqueous solutions by neutral acetate of lead.

Some tannic acids appear to be glucosides of gallic acid—i. e., ethereal compounds of the same with various sugars. They decompose into gallic acid and grape sugar upon boiling with dilute acids. Others contain phloroglucin instead of grape sugar. Common tannic acid, tannin, appears to be, at least in a pure state, not a glucoside but a digallic acid.

When the tannic acids are fused with potassium hydroxide they yield

mostly protocatechuic acid and phloroglucin.

Tannic Acid, Tannin, Digallic Acid, C₁₄H₁₀O₂ + 2H₂O, occurs in large quantity (upward of 50 per cent.), in gall-nuts (pathological concretions upon the different oak species, *Quercus infectoria*, produced by the sting of insects); in sumach (*Rhus coriaria*), in tea, and in other plants. It is prepared artificially by heating gallic acid with phosphorus oxychloride to 130°, or by boiling with dilute arsenic acid. Conversely, it passes, on boiling with dilute acids or alkalies, into gallic acid:

$$C_{14}H_{10}O_9 + H_2O = 2C_7H_4O_6$$

Pure tannin must, therefore, be considered a digallic acid (B. 17, 1478).

Tannin is best obtained from gall-nuts. The latter are finely divided and extracted with ether and alcohol. The solution separates into two layers, the lower of which is aqueous and contains tannin chiefly, and this is obtained by evaporation.

Pure tannic acid is a colorless, shining, amorphous mass, very soluble in water, slightly in alcohol, and almost insoluble in ether. Many salts—e. g., sodium chloride—precipitate it from its aqueous solutions, and it can also be removed from the latter by shaking with acetic ether. It reacts acid and is colored dark blue by ferric chloride (ink); gelatine precipitates it. Quantitative methods of estimating tannin are based on this behavior.

The penta-acetate, $C_{14}O_5(C_2H_3O)_5O_9$, heated to 210°, decomposes with formation of pyrogallol (p. 164).

Gallyl-gallic Acid, C14H10O9, a keto-tannic acid, forms an oxime and phenylhydra-

zone. See B. 22, R. 754; 23, R. 24.

The other tannic acids found in plants have been but little investigated; we may mention—

Kino-tannin, which constitutes the chief ingredient of kino, the dried juice of Partcarpus erinaceus and Coccoloba uvifera. Its solution is colored green by ferric salts. It yields phloroglucin on fusion with potassium hydroxide.

Catechu-Tannin occurs in catechin, the extract of Mimosa Catechu. Ferric salts color it a dirty green (p. 227). Catechin or Catechinic Acid, C₂₁H₂₂O₉ + 5H₂O, is also present in catechu. It crystallizes in shining needles.

Moringa-Tannin, C13H10O4 + H2O, Maclurin, is found in yellow wood (Morus time toria), from which it may be extracted (along with morin) with hot water. When the solution cools morin separates out; maclurin is precipitated from the concentrated liquid by hydrochloric acid, in the form of a yellow crystalline powder, soluble in water and al-cohol. Ferric salts impart a greenish-black color to its solutions. When fused with caustic potash it yields protocatechuic acid and phloroglucin. It forms pentacidyl de-Morin, C₁₃H₈O₆ + 2H₂O, decomposes into phloroglucin and resorcin. Nitric acid

oxidizes it to β -resorcylic acid. Consult B. 29, R. 646, for its constitution.

The Tannin of Coffee, C₃₀H₁₈O₃₆, occurs in coffee beans and Paraguay tea. Gelstine does not precipitate its solutions. Ferric chloride gives them a green color. It decomposes into caffete acid (see this) and sugar when boiled with potassium hydroxide. Pro-

tocatechuic acid is produced when it is fused with potassium hydroxide.

The Tannin of Oak is found in the bark (together with gallic acid, ellagic acid, quercite). It has the formula C₁₉H₁₆O₁₀, and is a red powder, not very soluble in cold water, but more readily in acetic ether. Ferric chloride colors its solution dark blue. Boiling, dilute sulphuric acid converts it into the so-called oak-red (phlobaphene),

C₃, H₁₆()₁₇ (?).
The *Timnin* found in the quinine barks is combined with the quinia-alkaloids. It closely resembles ordinary tannic acid, but is colored green by ferric salts. When boiled with dilute acids it breaks up into sugar and quina-red, an amorphous brown substance, yielding protocatechuic acid and acetic acid on fusion with potassium hydroxide.

2. POLYHYDRIC AROMATIC ALCOHOLS, IN WHICH ONLY ONE HYDROXYL IS PRESENT IN EACH SIDE-CHAIN, AND THEIR OXIDATION PRODUCTS.

t. DI- AND TRIHYDRIC AROMATIC ALCOHOLS.

Xylylene Alcohols, C₆H₄(CH₂OH)₂.—The three isomerides are obtained from the three corresponding xylylene chlorides or bromides by boiling with a soda solution. The ortho (1,2), called Phthalyl alcohol, is obtained also from phthalic acid chloride by reduction in glacial acetic acid with a large excess of sodium amalgam (B. 12, 646).

1,2-Phthalyl Alcohol melts at 62°; dichloride melts at 55°; the dibromide melts

at 95°.

1.3-Xylylene Alcohol melts at 46°; dichloride melts at 34°; the dibromide melts at 77°.

1,4 Xylylene Alcohol melts at 112°; dichloride melts at 100°; the dibromide melts

at 143°.

The three chlorides are formed when the xylenes are heated to 150° with PCl3 (B. 19, R. 24). The bromides are produced when bromine acts upon boiling xylenes (B. 18, 1281), or upon the latter in sunlight (B. 18, 1278). Tetrachlorxylylene Oxide, CoCl, (CH2)2O, melts at 218° (A. 238, 331). o-Xylylene Sulphide, CoH4(CH2)2S (B. 17, 1824).

o-Xylylendiamine, C₆H₄[1,2](CH₂NH₂)₂, is a liquid. It results when potassium phthalimide acts upon o-xylylene bromide (B. 21, 578), as well as by the reduction of phthalazine (p. 233). Upon heating, its chloride yields:

o-Xylylenimine, dihydroisoindol, C₆H₄(CH₂)₂NH, boiling at 213°. It also results in

the reduction of chlorphthalazine (B. 26, 2212)

Pseudocumenyl Glycol, CH₃[1]C₆H₃[2,4](CH₂OH)₂, melts at 77° (B. 19, 867). Mesitylene Glycol, CH₃[1]C₆H₃[3,5](CH₂OH)₃, boils at 190° (20 mm.). ω₂. Diamidomesitylene, CH₃. C₆H₃(CH₂NH₂)₃, boils at 268° (B. 25, 3017).

Mesitylene Glycerol, Mesicerine, CaH1[1,3,5](CH2OH)2, is a thick liquid (B. 16, 2509).

p-Di-a-oxethyl Bensene, CaH4[CH(OH)CH3], is a liquid obtained from p-diacetyl

benzene (B. 27, 2527).

The dihydric aromatic alcohols with the hydroxyl groups attached to two side-chains give rise to nine classes of oxidation-products, just as in the case of the aliphatic glycols (1, 290).

2. ALDEHYDE ALCOHOLS.

In this connection mention may be made of hydrophthalide, $C_6H_4\left\{\begin{bmatrix}1\\2\end{bmatrix}CH^9 \ge OH^4\right\}$ the reduction product of phthalide. It is a syrup, soluble in water. Dimethylhydrophthalide, $C_6H_4\left\{\begin{bmatrix}1\\2\end{bmatrix}C(CH_3)_3\right\}$ O, the reduction product of dimethylphthalide, melts at 89° (A. 248, 6i).

3. AROMATIC DIALDEHYDES.

Phthalic Acid Aldehydes, CaH4(CHO)2, corresponding to the three phthalic acids are obtained, like benzaldehyde from benzal chloride, by heating the xylylene tetrachlorides with water. o-Xylylene tetrachloride, or, better, o-xylylene tetrabromide and hydrazine yield phthalazine, C₆H₄ { CH: N (B. 28, 1830).

o-Phthalaldehyde melts at 52°; the dioxime melts at 245° (B. 20, 509). Isophthalaldehyde melts at 89°; the dioxime melts at 180° (B. 20, 2005). Terephthalaldehyde melts at 114°; the dioxime melts at 200° (B. 16, 2995).

The o-, m-, and p-xylylene tetrachlorides, C₆H₄(CHCl₂)₂, corresponding to the aldehydes, are prepared by heating the three xylenes with PCl₅ to 150-190°. The o-body melts at 89° and boils at 273°.

The m-body boils at 273°, and the p-compound melts at 93°. w-Tetrabrom-o-xylene melts at 116° (B. 28, 1830).

Oxydialdehydes are produced together with and from the oxymonaldehydes by means

of Reimer's reaction (p. 218). Thymodialdehyde, HO. $C_6H(CH_3)(C_3H_7)(CHO)_3$, melts at 79° (B. 16, 2104). Resorcindialdehyde, (HO)₂. $C_6H_7(CHO)_2$, melts at 127° (B. 10, 2212). a- and β -Orcendialdehydes, (HO)₂ $C_6H(CH_3)(CHO)_2$, melt at 118° and 168° (B. 12, 1003). a- and β -Oxyisophthalaldehyde, (HO)[4]C₈H₈(CHO)₂ and HO[2]C₈H₃(CHO)₂,

melt at 108° and 88° (B. 15, 2022).

4. DI- AND TRIKETONES.

Only one acidyl group can be introduced into benzene even by means of the aluminium

chloride synthesis.

p-Diacetylbenzene, C₆H₄[1,4](COCH₈)₂, melting at 114°, is formed by the action of dilute sulphuric acid upon terephthalyl dimalonic ester (B. 27, 2527). Diethyl Terephthaly!, C₆H₄(COC₂H₅)₉ (B. 19, 1850). Triacely! Bensene, C₆H₃[1,3,5](COCH₃)₈, melting at 163°, is formed by the benzene ring formation from formyl acetone (1, 319; 11, 42). In the benzene homologues containing methyl-groups in the meta-positions it is an easy matter, aided by Al₂Cl₈, to introduce acetyl residues between every two such methyl-groups. Thus, mesitylene, durene, and isodurene have given:

Diacetyl Mesitylene, C₈H(CH₃)₈(COCH₃)₃, melting at 40° and boiling at 310°;

diacetyl durene, melting at 178° and boiling at 323-326°, and diacetyl isodurene,

melting at 121° and boiling at 312-317° (B. 28, 3213; 29, 1413).

5. ALCOHOL CARBOXYLIC ACIDS.

Oxymethylbenzoic Acids, Carbinolbenzoic Acids.—There are three possible isomerides, and all of them have been prepared. They are isomeric with mandelic acid and the oxytoluic acids. o-Oxymethylbenzoic acid passes quite readily into the corresponding y-lactone, phthalide. Phthalide and meconine are the first lactones with which organic chemistry was enriched.

o-Oxymethylbenzoic Acid, Benzylalcohol-o-carboxylic acid, C₆H₄ { [1]CO, H melts at 120°, loses water and becomes phthalide, from which it is obtained by dissolving in caustic alkali and then precipitating with mineral acids.

Phthalide, o-Oxymethylbenzoic Acid Lactone, C₈H₄ { [1]CO >0, melting at 83° and boiling at 290°, was first made from o-phthalic acid. is formed (1) by heating o-oxymethylbenzoic acid or by allowing it to stand in contact with water (B. 25, 524); (2) by the reduction of phthalide chloride with zinc and hydrochloric acid (B. 10, 1445); (3) by the reduction of phthalic anhydride in acetic acid solution with zincdust (B. 17, 2178); (4) by the action of bromine vapor upon orthotoluic acid at 130-140°; (5) from xylylene dichloride upon boiling with water and lead nitrate; (6) by decomposing nitrosophthalimidine obtained from phthalimide with caustic potash (A. 247, 291); or (7) by treating o-cyanbenzyl chloride in glacial acetic acid with hydrochloric acid at 100° (B. 25, 3021).

It is reduced to orthotoluic acid on boiling with hydriodic acid. Potassium permanganate oxidizes it to phthalic acid. See also phthalaldehydic acid (p. 236), phthalic acid and ω-cyan-o-toluic acid (p. 244). Phenylhydrazine adds itself to phthalide (B. 26, 1273). Numerous derivatives have been obtained from o-oxymethylbenzoic acid, some of

which, like the acid itself, change over to heterocyclic compounds.
o-Chlormethylbenzoic Acid, Cl. CH₂[2]C₆H₄CO₂H. The free acid is not known. Its ethyl ester results from the action of alcohol upon its chloride.

It boils at 141° (12 mm.), and also without decomposition at 245° (760 mm.).

o-Chlormethyl Benzoyl Chloride, Phthalide Chloride, ClCH₂[2]C₆H₄. COCl, boiling at 135° (12 mm.), results when PCl₅ acts upon phthalide at 55-60°.

o-Chlormethylbenzamide, ClCH₂[2]C₆H₄. CONH₂, melts with decomposition at 190° (see pseudophthalimidine). It is produced on conducting dry ammonia into an otherwale solution of phthalide phlatic and the state of the sta ethereal solution of phthalide chloride solution, and by the action of sulphuric acid upon

o-Chlormethyl Benzanilide, Cl. CII₂[2]C₆H₄CONHC₈H₅, melts at 115°.

o-Chlormethyl Benzonitrile, o-Cyanbenzyl Chloride, Cl. CII, [2]C, H, CN, melting at 252°, is formed upon conducting chlorine into boiling o-tolunitrile (p. 203) (It. 20, 2222). The corresponding o-Cyanbenzyl alcohol is known only in its ethers (B. 25, 3018).

Phthalide yields the base Phthalimidine, $C_0H_4\left\{\begin{bmatrix}\mathbf{I}\\\mathbf{Z}\end{bmatrix}CO_2\right\}NH$, when it is heated in an atmosphere of ammonia. It can also be very readily obtained by reducing phthalimide with tin and hydrochloric acid (A. 247, 291); from o-cyanbenzylamine with nitrous acid, and from phthalide chloride by the action of alcohol and ammonia. It melts at 150° and boils at 337°.

Nitrosophthalimidine, C8H6ON. NO, melts at 156°. Pseudophthalimidine, C_6H_3 $\left\{\begin{bmatrix} I \\ 2\end{bmatrix}CH_2 \\ O \end{bmatrix}$, is an oil. In contact with water it is resolved into phthalide and ammonia. Its hydrochloride is formed when o-chlormethyl-benzamide is heated to 130°-140°.

Phthalide Anil, Phenylphthalimidine, Coll, \[\bigcolum_{2\text{Coll}_2\text{Cll}_2} \] NCoH, melting at 160%,

MECONINE.

235

results on heating phthalide and aniline to 200-220°, upon reducing phthalanil with tin and hydrochloric acid, and by distilling o-chlormethylpenzanlide under diminished pressure. o-Cyanbenzylamine, NH₂. CH₂[2]C₄H₄CN, is a colorless oil, which becomes crystalline. It is formed when o-cyanbenzyl chloride acts upon potassium phthalimide (B. 20, 2233).

Thiophthalide, C_6H_4 $\left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix} CO \\ 2 \end{bmatrix} CH_3 > S$, melts at 60° (A. 257, 298), and—

Selenophthalide, C₆H₄ { [1]CO Se, melts at 58° (B. 24, 2596). Phthalides, substituted in the benzene nucleus, are also known; they have been mostly obtained from substituted o-phthalic acids. Mention may be made of:

p-Nitrophthalide, $NO_{1}C_{0}H_{3}\left\{\begin{bmatrix}1\\2\end{bmatrix}CO_{2}\right\}$ O, melting at 135°. It is produced when Chromic acid and glacial acetic acid act upon o-nitronaphthalene (A. 202, 219).

p-Oxyphthalide, HO. C₆H₅ { [1]CO > O, melting at 222° (A. 233, 235), is obned from pove-orbibalic call tained from p-oxy-o-phthalic acid.

Meconine, 5,6-Dimethoxyphthalide, (CH₈O)₂[5,6]C₈H₂ { [1]CO | 2]CH₂>O, melting at **202°**, is the lactone of meconinic acid, which is only stable in the form of its salts. Its name is derived from the Greek word μήκων, signifying poppy.

Meconine occurs already formed in opium, where Couerbe discovered it in 1832, and is obtained on boiling narcotine with water (Wöhler and Liebig, 1832). It may be formed from opianic acid (p. 237), the corresponding aldehyde acid, just like phthalide from phthalaldehydic acid, by reduction with sodium amalgam and precipitation with acids. It was the first lactone known to chemistry. It dissolves in the alkalies, yielding salts of meconinic acid. In the same manner that phthalimed yields phthalide (p. 234), hemipinimide furnishes \u03c4-meconine, and not meconine (B. 20, 883).

$$\begin{array}{cccc} C_6H_4\left\{ \begin{bmatrix} 1\\2 \end{bmatrix}CO_2 > O & C_6H_4\left\{ \begin{bmatrix} 1\\2 \end{bmatrix}CO_2H & (CH_3O)_2C_6H_2\left\{ \begin{matrix} CO\\CH_2 \end{matrix} \right\} > O & (CH_3O)_2C_6H_2\left\{ \begin{matrix} CHO\\CO_2H \end{matrix} \right\} \\ & \text{Phthalide} & \text{Meconine} & \text{Opianic Acid.} \end{array} \right.$$

ψ-Meconine, 3,4-Dimethoxyphthalide, (CH₈O)₉[3,4]C₆H₂{[1]CO₂>O, melts at 132°. It is made from hemipinimide, just as phthalide is formed from phthalimide (B. 20, 884).

o a-Oxyethylbenzoic Acid Lactone, a-Methylphthalide, $C_6H_4\{\begin{bmatrix} I\\ 2\end{bmatrix}CH>0$, boils at 275°. It is formed in the reduction of acetophenone-o-carboxylic acid (p. 238) with sodium amalgam. Hydriodic acid and phosphorus reduce it to o-ethylbenzoic acid (B. 29, 2533).

Dimethyl Phthalide, 0- β -oxyisopropylbenzoic acid lactone, C_6H_4 $\begin{bmatrix} 1 & CO \\ 2 & CCH_3 \end{bmatrix}$, melting at 67° and boiling at 270°, was made by the action of zinc-dust and methyl

iodide upon phthalic anhydride (A. 248, 57).

m Oxymethylbenzoic Acid is only known in the form of its alcohol anhydride, chloride, Cl. CH₁[3]C₄H₄CN, melting at 180°, which is formed from m-cyanbenzyl chloride, Cl. CH₁[3]C₄H₄CN, melting at 67° and boiling at 259°, the reaction-product of chlorine upon m-tolunitrile (p. 203). ω-Chlor-m-toluic Acid melts at 135°, and m-Benzylamine Carboxylic Acid, NH₄CH₂[3]C₄H₄CO₂H, melting at 181°, is obtained (1) from p-carbinol bromide benzoic acid, Br. CH₂[4]C₆H₄CO₂H, (A. 162, 342);

(2) by the action of concentrated sodium hydroxide upon terephthalaldehyde (A. 231,

372).

p-Cyanbenzyl Alcohol, HOCH₂[4]C₈H₄CN, melting at 133°, is prepared from p-cyanbenzyl chloride, melting at 79° and boiling at 263°, by the action of potassium

carbonate. p-Chlormethylbenzamide, CH₂Cl[4]C₈H₄CONH₂, melts at 173°. p-Chlormethylbenzoic Acid, CH₂Cl[4]C₈H₄CO₂H, melts at 199° (B. 24, 2416). m. and p-Oxyisopropylbenzoic Acids, (CH₂)₂C(OH). C₈H₄. CO₂H, melting at 123° and 155°, result when m-isocymene (A. 275, 159), and cymene, from cumic acid, are oxidized with potassium permanganate. The 3-amido-4-oxyisopropylbenzoic acid, derived from the p-acid, changes under the influence of carboxylic anhydrides into assections of the contraction of the conic acids (see these).

6 ALDEHYDE ACIDS.

o-Phthalaldehydic acid and 5,6-dimethoxy-o-phthalaldehydic acid, or opianic acid, are the most important representatives of this class. In the phthalaldehyde acids the aldehyde group occupies the 7-position with reference to the carboxyl group. Like the aliphatic y-ketonic acids (the lævulinic acids, 1, 379), the phthalaldehyde acids form monoacetyl derivatives, whose existence and deportment argue more strongly for the γ-oxylactone formula (Liebermann, B. 19, 765, 2288) than the carboxylic acid formula of such acids:

$$\begin{array}{c} \operatorname{CH}_2,\operatorname{CO}_2\operatorname{H} & \operatorname{CH}_2,\operatorname{CO} \\ \operatorname{CH}_2,\operatorname{CO},\operatorname{CH}_3 & \operatorname{CH}_2-\operatorname{COH} \\ \operatorname{CH}_2 & \operatorname{CO},\operatorname{CH}_3 & \operatorname{CH}_2-\operatorname{COH} \\ \operatorname{Cet}_3 & \operatorname{Ceth}_4 \end{array} \\ \begin{array}{c} \operatorname{C}_6\operatorname{H}_4 \\ \operatorname{C}_2\operatorname{CH} & \operatorname{OPhthaladdehydic Acid.} \end{array} \\ \begin{array}{c} \operatorname{C}_6\operatorname{H}_4 \\ \operatorname{Ceth}_3 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_3 & \operatorname{Ceth}_4 \end{array} \\ \begin{array}{c} \operatorname{Ceth}_4 \\ \operatorname{Ceth}_3 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_3 & \operatorname{Ceth}_4 \end{array} \\ \begin{array}{c} \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_3 & \operatorname{Ceth}_4 \end{array} \\ \begin{array}{c} \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \end{array} \\ \begin{array}{c} \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \end{array} \\ \begin{array}{c} \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \end{array} \\ \begin{array}{c} \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \end{array} \\ \begin{array}{c} \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \end{array} \\ \begin{array}{c} \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \end{array} \\ \begin{array}{c} \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \end{array} \\ \begin{array}{c} \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4 & \operatorname{Ceth}_4 \\ \operatorname{Ceth}_4$$

Opianic acid forms two series of esters. Their difference is due to the fact that the one series represents carboxylic esters, while the other series consists of y-oxylactore

The deportment of the oxime anhydrides of phthalaldehydic acid and opanic acid is worthy of note. They change to the corresponding phthalimides with an appreciable evolution of heat, when they are gently heated. The phthalaldehydoxime anhydridic acid first changes to o cyanbenzoic acid, which yields phthalimide upon fusion. The determination of the heat of combustion of opian-oximic acid anhydride and hemipinimide has shown that in the conversion of the former into the latter the quantity of heat set free (52.6 Cal. for the gram-molecule) was tenfold greater than the molecular rearrangement-energy of allocinnamic into cinnamic acid, and eight times that observed in the conversion of maleic into fumaric acid (B. 25, 89).

o Phthalaldehydic Acid (formulas above), melting at 97°, is formed (1) upon heating bromphthalide (see below) with water; (2) by heating ω -pentachlor-o-xylene and (3) o-cyanbenzal chloride with hydrochloric acid (B. 30, 3197). Hydrazine converts the acid into phthalazone (see this) C_6H_4 [1]CO — NH, melting at 183°; phenylhydra-

zine changes it to phenylphthalazone, melting at 105° (B. 26, 531), and hydroxylamine. in aqueous solution, into benzaldoxime-o-carboxylic acid, melting at 120°; while in alcoholic solution the product is benzaldoxime-o-carbonic anhydride, benzo-ortho-oxazinone, melting at 145°. The latter at 145° rearranges itself with evolution of much heat into o-cyanbenzoic acid, which at more elevated temperatures becomes phthalimide (B. 26, 3264):

$$\begin{array}{c} C_6H_4 \begin{cases} [1]COOH \\ \\ [2]CH = NOH \end{cases} \\ \text{Benzaldoxime-o-Carboxylic} \\ \text{Acid} \\ \end{array} \begin{array}{c} C_6H_4 \begin{cases} [1]COO \\ \\ [2]CHN \end{cases} \\ \text{Benzaldoxime-o-Carboxylic} \\ \text{Carboxylic Acid} \\ \text{Anhydride} \\ \end{array} \begin{array}{c} C_6H_4 \begin{cases} [1]COOH \\ \\ [2]C = NOH \\ \text{O-Cyanbenzoic} \\ \text{O-Phthallmide.} \\ \text{O-Phthallmide.} \\ \end{array}$$

Methoxyphthalide, phthalaldehydic methyl ether, melting at 44°; ethoxyphthalide melting at 66°, and amidophthalide, amide of phihalaldehydic acid, are produced by the action of methyl and ethyl alcohol, and of ammonia upon bromphthalide, or the bromide of phthalaldehydic acid, melting at 85°, produced when bromine vapor acts upon phthalide at 140°. Aceto-phthalaldehydic acid, acetoxyphthalide, is formed by

the interaction of acetic anhydride and phthalaldehydic acid.

Diphthalide Ether, C_6H_4 $\left\{ \begin{bmatrix} 1 \end{bmatrix} CO \\ \begin{bmatrix} 2 \end{bmatrix} CH \end{bmatrix} C_6H_4$, melting at 221°, is formed from o-phthalaldehydic acid and bromphthalide. In accordance with the double formulation of phthalaldehydic acid (see above) two views may be held in regard to its various derivatives:

The idea that acetoxyphthalide and the diphthalide ethers are anhydrides of carboxylic acids is very improbable. Phthalaldehydic acid and opianic acid react especially readily, even in the cold, with amines. Water is eliminated. The resulting bodies dissolve in part very easily in soda, and in part with difficulty, hence are in part derived from the amidophthalide and partly from the imidoaldehydic acid formula (B. 29, 174, **≥**030).

$$C_6H_4\Bigl\{\begin{bmatrix}1\\2\end{bmatrix}CO>O\\CH-NHR \qquad \text{and} \quad C_6H_4\Bigl\{\begin{bmatrix}1\\2\end{bmatrix}COOH\\2\end{bmatrix}CH=NR.$$

Phthalaldehyde Chlorides: Penta-chloride of o-Phthalaldehydic Acid, n-Penta-chlor-o-xylene, CHCl₂[2]C₆H₄CCl₂, melting at 53°, results when PCl₅ acts upon o-xylene at 140°. o-Cyanbenzal Chloride, nitrile of o-phthalaldehyde-chloride acid, CHCl₂-[2]C₈H₄CN, boiling at 260°, is formed by the action of chlorine upon boiling o-cyantoluene (B. 30, 3197).

Noropianic Acid, 5,6-dioxyphthalaldehydic acid, (HO), C6H4(CHO)COOH, melting at 171°, is obtained from opianic acid, together with isovanillin and carbon dioxide, upon

heating with hydriodic acid. It is colored bluish-green by ferric chloride.

Opianic Acid, 5,6-dimethoxyphthulaldehydic acid, (CII₃O)₈[5,6]C₆H₂[2]CHO.-CO₂H, melting at 150°, is produced on oxidizing narcotine with dilute sulphuric acid and MnO₂ (1842, Wöhler and Liebig, A. 44, 126). Meconine is formed in its reduction. When it is evaporated with caustic potash it changes in part to meconine and partly to bemipinic acid. just as benzaldehyde yields benzyl alcohol and benzoic acid. It is oxidized to hemipinic acid (p. 241). Upon heating with hydrochloric acid there results at first: 5-Methoxy-6-oxyphthalaldehydic acid, methyl noropianic acid, (CH₃0)[5](HO)[6]-C₆H₂(CHO)CO₂H, melting at 154° (B. 30, 691), while under more intense heat isovanillin and CO₃ are the products. Concentrated sulphuric acid converts opianic acid into rustopin (see this), a tetraoxyanthraquinone derivative.

Opianic acid behaves toward hydrazine, phenylhydrazine, and hydroxylamine just like phthalaldehydic acid (p. 236). Dimethoxyphthalazone, opiazone, melts at 162°, when it is anhydrous (B. 27, 1418). Phenylopiazone melts at 175° (B. 19, 2518). Opianoximic Acid, melting at 82°, becomes, on boiling its aqueous solution, the anhydride of opianoximic acid, melting at 114°. When this is heated alone, or when its alcoholic solution is boiled, hemipinimide results as a consequence of rearrange-

ment (B. 24, 3264).

Esters.—Opianic acid forms two series of alkyl esters, corresponding to the carboxylic-and to the y-oxylactone formulas of the acid (p. 236). The one series, the true carboxylic esters, are stable in the presence of water. They are formed by the action of alkyl iodides upon the silver salt or of alcohols upon the chloride of opianic acid.

They manifest the typical aldehyde reactions (B. 29, R. 507). The second series, the γ -oxylactones or ψ -esters, are formed on boiling opianic acid with alcohols: Methyl Opianic Ester, $(CH_2O)_2C_3H_2(CHO)CO_2CH_3$, melts at 82° and boils at 233°

(51 mm.). The ethyl ester melts at 64°. ψ-Methyl Opianic Ester,

(CH₃O)₃C₆H₂ O , melts at 103° and boils at 238° (52 mm.). The vethyl cO—OCH₃ ester melts at 92° (B. 25, R. 907; 26, R. 700). Acetyl-opianic Acid melts at 120° (B. 19, 2288). [3]-Nitro-opianic Acid, melting at 166°, yields by reduction dimethoxyanthranilcarboxylic acid, azoopianic acid, which upon treatment with acetone and sodium hydroxide forms an indigo derivative (compare anthranil, p. 212). Pseudo-opianic Acid, (CH₃O)₃[3,4]C₆H₃[2](CHO)CO₂H, melting at 121°, is formed from berberal, an oxidation product of the alkaloid berberine (see this), when it is boiled with dilute sulphuric acid. Amidoethylpiperonylcarboxylic anhydride (B. 24, R. 155) is formed simultaneously. The oxime, melting at 124°, is rearranged upon heating into

hemipinimide (B. 24, 3266).

m-Aldehydo-benzoic Acid, Isophthalaldehydic acid, CHO[3]C₈H₄CO₃H, melts at 165°.

m-Cyanbenzaldehyde melts at 80°.

m-Cyanbenzal Chloride boils at 74° (B. 24, 2416).

p-Aldehydo-benzoic Acid, Terephthalaldehydic Acid, CHO[4]C₃H₄.

CO₂H, melts at 285°.

p-Cyanbenzaldehyde melts at 97°.

p-Cyanbenzal Chloride

boils at 275° (B. 24, 2422).

Mono and dioxyaldehydo-acids have been obtained from mono- and dioxycarboxysic acids by means of chloroform and caustic alkali (B. 12, 1334; 16, 2182).

7. KETONE CARBOXYLIC ACIDS.

o-Acetophenone carboxylic acid is the most important of the aromatic monocarboxylic acids with keto- and carboxyl-groups in different side-chains. In it the γ-position imparts to the keto- and carboxyl groups reactions similar to those manifested by o-phthaladlehydic acid (p. 236). Hence in addition to the carboxylic acid formula we must also consider the γ-oxylactone formula for o-acetophenone carboxylic acid. Its acetyl compound must be viewed as acetyl-γ-oxylactone:

$$C_6H_4$$
 [1]COOH or C_6H_4 [1]CO>O C_6H_4 [2]C(OH)CH, C_6H_4 [2]C(OCOCH,)CH,

o-Acetophenone Carboxylic Acid, o-Acetobenzoic Acid, melting at 115°, is isomeric with benzoyl acetic acid (see this) and tolylglyoxylic acid (see this). It has a sweet taste, and is formed on boiling benzoyl aceto-o-carboxylic acid with water (B. 26, 705; 29. 2533). The acetyl compound melts at 70° (B. 14, 921). Hydrazine converts it into methylphthalazone, melting at 222° and boiling at 247° (B. 26, 705). With phenylhydrazine it yields methyl-n-phenylphthalazone, melting at 102° (B. 18, 803). Its ethyl ester and hydroxylamine form an oxime anhydride, melting at 158° (B. 16, 1995).

Various homologous o acidylbenzoic acids have been obtained by digesting their anhydrides, the alkylidene phthalides, with potassium hydroxide. These anhydrides are produced in the condensation of phthalic anhydride and fatty acids, when water and carbon dioxide are eliminated: o butyrophenone carboxylic acid and o isovalerophenone

carboxylic acid melt at 89° and 88° (B. 29, 1437).

P-Acetophenone Carboxylic Acid melts at 200°. It results from the oxidation of p-B-oxylicopropylbenzoic acid (A. 219, 260). p-Cyanacetophenone, melting at 60°, is made from p-amido-acetophenone (B. 20, 2055).

Polycarboxylic Acids.—Three varieties are to be distinguished in each group of these acids: those in which all the carboxyl groups are directly joined to the benzene nucleus; those in which these groups are in part joined to the nucleus and are in part present in the side-chains; and, lastly, those in which all of the carboxyl groups are contained in the side-chains—e. g.:

 C_6H_4 $\begin{cases} COOH \\ COOH \end{cases}$ Phthalic Acids

 C_6H_4 $\left\{ egin{array}{c} CH_2 \ . \ CO_2H \ CO_2H \ Homophthalic Acids \end{array}
ight.$

C₆H₄ { CH₂ · CO₂H CH₂ · CO₂H Phenylene Diacetic Acids.

& DICARBOXYLIC ACIDS.

(a) Phthalic Acids are the final oxidation products of all benzene derivatives in which two hydrogen atoms of the benzene nucleus have been replaced by side-chains. Hence, they are of importance in determining the position of these two side-groups in the benzene nucleus (p. 35). Their hydrogen addition products, the hydrophthalic acids, are also very important compounds from a theoretical standpoint. Again, o-phthalic acid is distinguished from the m- and p-bodies by its ability to form an anhydride and other cyclic derivatives. In addition to the dicarboxyl formula, the γ -dioxylactone formula has been taken into consideration for this acid. It is applied technically in the manufacture of phthalein dye-substances, which are of great value. The phthalic acids bear the same relation to the phthalyl alcohols, the phthalaldehydes, oxymethylbenzoic acids, and phthalaldehydic acids that oxalic acid sustains to ethylene glycol, glyoxal, glycollic acid, and glyoxalic acid:

CH ₂ OH	СНО	COOH	COOH	COOH
сн.он	сно	сн,он	сно	соон
Glycol	Glyoxal	Glycollic Acid	Glyoxalic Acid	Oxalic Acid
$C_{\bullet}H_{\bullet}$ $CH_{\bullet}OH$	$C_{\bullet}H_{\bullet}$ $\begin{cases} CHO \\ CHO \end{cases}$	$C_{\bullet}H_{\bullet} \begin{cases} COOH \\ CH_{\bullet}OH \end{cases}$	$C_{\bullet}H_{\bullet}$ $\begin{cases} COOH \\ CHO \end{cases}$	$C_6H_4\begin{cases} COOH \\ COOH \end{cases}$
CHOH	CHO	CHOH	CHO	
Phthalyl Alcohol	Phthalaldehyde	Oxymethyl-	Phthalaldehydic	Phthalic Acids.
		benzoic Acids	Acids	

Phthalic Acid, Benzene - o - dicarboxylic Acid, C₆H₄ [1]COOH [2]COOH' C₆H₄ (CO) O (A. 269, 155), melts, when rapidly heated, at 213°, decomposing at the same time into the anhydride and water. It is obtained by oxidizing naphthalene and tetrachlornaphthalene with nitric acid. It is made technically in large amounts. It also results on oxidizing o-xylene and o-toluic acid with potassium permanganate, alizarin and purpurin with nitric acid, or with manganese dioxide and sulphuric acid; and in slight amount in the oxidation of benzene and benzoic acid. It cannot be prepared by using chromic acid as an oxidizing agent, since the latter burns it at once to carbon dioxide. It can be synthetically obtained from o-nitrobenzoic acid by converting the latter into o-cyanbenzoic acid and then boiling this with alkalies (p. 241).

History.—Laurent first obtained the acid, in 1836, by oxidizing naphthalene tetrachloride. He considered it a naphthalene derivative and named it naphthalinic acid (A. 19, 38). After Marignac had deduced the correct formula, C₈H₈O₄ (Å. 38, 13), and demonstrated that the acid was not a derivative of naphthalene, Laurent gave it the name phthalic acid (A. 41, 107).

When heated with an excess of calcium hydroxide it yields benzene and 2CO₂. Only ICO₂ is split off and calcium benzoate produced if its lime salt be heated to 330-350°

with one molecule of Ca(OH).

Sodium amalgam converts phthalic acid into di-, tetra-, and hexa-hydrophthalic acids. Esters.—As the investigation of phthalyl chloride seemed to assign a lactone formula to this body, in which the two chlorine atoms were attached to the same carbon atom, search was made for two series of esters. However, the action of alkyl iodides upon the silver salt, and that of alcohols upon the chloride, produced the same esters (A. 238, 318).

If we disregard intramolecular atom-rearrangement, this behavior would argue for corresponding formulas for the chloride and silver salt. The methyl ester boils at 280°, and the ethyl ester at 288° (B. 16, 860). These esters condense with acetic ester, acetone, and similar bodies in the presence of sodium ethylate, forming diketshydrindene denvatives. The phenyl ester melts at 70° (B. 7, 705; 28, 108). The ethyl ester acid is a heavy oil.

Chlorides.—The chloride of the ethyl ester-acid is a decomposable oil, produced when

PCl₃ acts upon the ethyl ester-acid (B. 20, 1011).

Phthalyl Chloride, C₆H₄ { [1]COCl or C₆H₄ { [1]CO₂ > 0, solidifies at 0° and boils at 275°. It results upon heating the anhydride for several hours with an equinolecular quantity of PCl₅ at 200° (A. 238, 329). The conversion of phthalyl chloride with glacial acetic acid and sodium amalgam into 0-phthalyl alcohol is an argument favoring the sym. formula (p. 232). The unsym. formula is evident from conversion of the chloride by sinc and acetic acid into phthalyle (p. 222) diphthalyl conversion of the chloride by zinc and acetic acid into phthalide (p. 233), diphthalyl, C₆H₄ C_C C_C C_C C_C C₆H₄, and hydrodiphthalyl, and with benzene and aluminium chloride into phthalophenone or diphenylphthalide.

Phthalylene Tetrachlorides. - PCl, converts phthalyl chloride into phthalylene tetrachloride, melting at 88°, and phthalylene tetrachloride, melting at 47°. These cannot be changed into one another. Their crystals have been measured. Both yield phthalic acid and have been assigned the formulas C_6H_4 $\left\{ \begin{array}{l} CCl_9\\ COCl_4 \end{array} \right\}$ and C_6H_4 $\left\{ \begin{array}{l} CCl_9\\ CCl_4 \end{array} \right\}$ 0. The formation of the two chlorides is only comprehensible from the unsymmetrical phthalyl chloride formula (B. 19, 1188). The chloride, melting at 88°, is also obtained in the action of PCl₅ upon phthalide chloride (p. 234). This reaction argues for the unsymmetrical formula, just as well as the conversion into diphenylanthrone (see this) by condensation with benzene by means of Al₂Cl₆ or concentrated sulphuric acid (B. 28, R. 772).

Phthalic Anhydride, C₆H₄ { [1]CO > O, melting at 128° and boiling at 284°, sublimes readily in long needles. It results upon fusing phthalic acid or digesting it with acetyl chloride (B. 10, 326). Phthalic anhydride yields condensation products 45

readily as benzaldehyde:

Thus, phthalyl acetic acid is formed on boiling the anhydride with acetic anhydride. It reacts in like manner with malonic ester and acetoacetic ester. At more elevated temperatures it combines with homologous fatty acids, with the elimination of CO, and the formation of alkylidene phthalides. It condenses with phthalide to diphthalyl (see this). With the phenols it yields the important phthalein dyes (see these), a group of triphenylmethane dyes, comprising certain beautifully fluorescent compounds. Thiophthalic Anhydride, $C_6 H_1(CO)_2 S$, melts at 114° and boils at 284° (B. 17, 1176). Phthalyl Superoxide, $C_6 H_1(CO)_2 S$, melts at 133° , giving gas evolution. When heated rapidly to 136° it explodes. It is formed when phthalyl chloride is acted upon with a sodium peroxide solution (B. 27, 1511).

Phthalamic Acid, C_6H_4 { $\begin{bmatrix} I \ COOHI \\ 2 \end{bmatrix} COOHI \\ 0 \end{bmatrix}$ or C_6H_4 { $\begin{bmatrix} I \ COHI_2 \end{bmatrix} COHI_3$ O, melting at 148°, is formed from the anhydride and ammonia, or when baryta-water acts upon Phthalimide (B. 19, 1402). Anilic Acid melts at 192°. Phthalic Diamide, C_6H_4 $\left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}C(NH_2)_2 > 0, \text{ melts at 140 - 160°, changing at the } C_6H_4 \right\} \left\{ \begin{bmatrix} 2\end{bmatrix}CO - 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CONH_2 + 1, \text{ or } C_6H_4 \right\} \left\{ \begin{bmatrix} 1\end{bmatrix}CO$ same time to phthalimide. It is produced when ammonia acts upon the ester (B. 19. 1399; 21, R. 612; 24, R. 320; 25, R. 911).

Phthalimide, C_6H_4 $\left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}CO > NH$ or C_6H_4 $\left\{ \begin{bmatrix} 1 \\ 2 \end{bmatrix}CO = NH \right\} > O$, melting at 238°, is about 1

is obtained:

By heating phthalic anhydride or chloride in ammonia gas;

By heating phthalic acid with ammonium sulphocyanide (B. 19, 2283); from phthalamide, and

By the molecular rearrangement of the isomeric o-cyanbenzoic acid (p. 236).

It forms potassium phthalimide, C₆H₄(CO)₂NK, by the action of alcoholic potash. Salts of the heavy metals can be obtained from it by double decomposition. Potassium phthalimide is readily rearranged or transposed with organic halogen derivatives, consequently it is frequently employed in the preparation of numerous amines (p. 162). While by this means alkylogens yield symmetrical alkylimides of the formula $C_6H_4(CO)$ -NR,—e. g., s-methyl- and benzylphthalimide, melting at 132° and 115°,—unsymmetrical alkylimides of the formula $C_6H_4\left\{ \begin{array}{c} C:(NR)\\ CO \end{array} \right\}$ O are obtained from the interaction of phthalalkylamic acids and acetyl chloride: unsym. methyl- and bensylphthalimide melt at 78° and 81° (B. 27, R. 737).

Reduction changes phthalimide to phthalimidine (p. 234), while bromine and caustic potash convert it into anthranilic acid (p. 211).

Phthalanil, C₆H₄(CO)₂NC₆H₅, melts at 203°. It is obtained from phthalic acid and aniline; also upon boiling o-benzoylbenzoic acid with aniline hydrochloride (B. 26, 1261). Phthalylphenylhydrazide, C₆H₅(CO)₂(NHNHC₆H₅)₂, melts at 161°. Phthalylhydrazine, C₆H₄(CO)₂(NH)₃, from phthalic anhydride and hydrazine hydrate, sublimes at 200°. Phthalimide and hydrazine yield an isomeric phthalhydrazine (B. 28, R. 429; 29, R. 987).

a-Phthalylphenylhydrazine, C₆H₄(CO), N. NHC₆H₅, melts at 178°.

β-Phthalylphenylhydrazine, C₆H₄ CONH
CONC₆H₅, melts at 210° (B. 19, R. 303; 20, R. 255). Phthalylhydroxamic Acid, CaH, CaO, NOH, melts at 230° (B. 16, 1781;

28, R. 998).

Nitriles of Phthalic Acid: o Cyanbenzoic Acid is produced when anthranilic acid is treated with nitrous acid and cuprous cyanide. It rearranges itself, upon the application of heat, into phthalimide (B. 18, 1496; 19, 2283; 25, R. 910). o Cyanbenzoic Acid Ester melts at 70° (B. 19, 1491). o-Cyanbenzotrichloride, CN[2]C₆H₄CCl₃, melting at 94° and boiling at 280°, is obtained from o-tolunitrile (B. 20, 3199). o-Phthalonitrile, C₆H₄[1,2](CN)₃, melting at 141°, is obtained from o-amidobenzonitrile through the diazo-compound (B. 29, 630).

Substituted o-Phthalic Acids.—Substituted naphthalenes and substituted toluic acids yield substituted phthalic acids when they are oxidized. Tetrachlorphthalic Acid, C₆Cl₄(CO₂H)₂, melts with anhydride formation at 250°. It is obtained from pentachlornaphthalene (A. 149, 18). Once different ethyl esters were obtained on the one hand from the chloride, and on the other from the silver salt (A. 238, 326); the ordinary ester

melting at 60°, and another melting at 124°.

3- and 4-Iod-o-phthalic Acids melt at 206° and at 182° (B. 29, 1575, R. 792). Tetraiod-o-phthalic Acid melts at 324-327° (B. 29, 1634). 3- and 4-Nitro-o-phthalic Acids melt at 219° and 161°. 3- and 4-Amido-o-phthalic Acids (A. 208, 245). Sulpho-o-phthalic Acid is obtained by heating naphthols, naphthylamines, and naphthalene sulphonic acids with concentrated sulphuric acid and mercury to 220-300° (B. 29, 2806).

Oxy-o-phthalic Acids.—They are recognized by the melting points of their an-

hydrides, into which they change upon the application of heat.

3-Oxy-o-phthalic Acid Anhydride melts at 147° (B. 16, 1965). Dinitro-3-oxyo phthalic Acid is juglonic acid, which can also be obtained by the action of nitric acid upon juglone, a naphthalene derivative (B. 19, 168). 4 Oxy o phthalic Acid Anhy-

dride melts at 165° (A. 233, 232).

Norhemipinic Acid., 3,4-Dioxyphthalic Acid Anhydride, melting at 238°, is produced when 3,4-dichlormethoxyphthalic acid anhydride, (CICH₂O)₂C₆H₄(C())₂O, melting at 156°,—the reaction product of PCl₅ and hemipinic acid at 180°,—is digested with water. Hemipinic Anhydride, 3,4-dimethoxyphthalic anhydride, melts at 167°. The acid is formed, together with opianic acid and meconine, in the oxidation of marcotine; also with meconine on fusing opianic acid with caustic potash:

Consult B. 29, R. 96, for the hemipinamido-acids and the hemipinimides.

6-Amidohemipinic Acid is produced on boiling its anhydride with baryta-water.

The anhydride is azo-opianic acid or 2,3-dimethoxy-5,6-anthranilcarboxylic acid,

(CII₃O)₂C₈H(CO₂II) { CO | NH | (p. 238).

Normetahemipinic Anhydride melts at 247°. Metahemipinic Anhydride melts at 175°. Metahemipinic Acid or 4,5-Dimethoxy-o-phthalic Acid was obtained in the decomposition of papaverine (B. 24, R. 902). Methylene Metahemipinic Ether Acid, (CH₂O₂)C₆H₂(COOH)₂, is hydrastic acid, formed in the oxidation of hydrasticine. The oxidation of cotarnine yields cotarnic acid or methylene methyl-ether—3,4,5-trioxy-o-phthalic acid, (CH₂O₂)(CH₂O)C₆H(COOH)₂.

Isophthalic Acid, Benzene-m-dicarboxylic Acid,

C₄H₄ { [1]CO, H, melts above 300° and sublimes. It is formed by oxidizing m-xylene (p. 54) and m-toluic acid with a chromic acid mixture; by the further oxidation of m-phthalyl alcohol ethyl ether, obtained from m-xylylene bromide and alcoholic potash (B. 21, 47), and from m-dicyanbenzene and m-cyanbenzoic acid (p. 242). The last two methods permit of nucleus-syntheses from the corresponding amido-compounds, m-phenylenediamine and m-amidobenzoic acid.

The acid is also formed when potassium m-sulpho-benzoate, m-brom-benzoate, and benzoate are fused with potassium formate (terephthalic acid is also formed in the last two cases); by the action of the ester of chlorcarbonic acid and sodium amalgam upon m-dibrombenzene; also by heating hydro-pyromellitic and hydro-prehnitic acids (p. 246).

Isophthalic acid is soluble in 460 parts boiling and 7800 parts cold water. It does not yield an anhydride. Reduction changes it to tetrahydroisophthalic acid. The barium sall, $C_6H_4(CO_2)_2Ba + 6H_2O$ (A. 260, 30), is very soluble in water (distinction between phthalic and terephthalic acids).

The Dimethyl isophthalate melts at 64°.

Isophthaly! dichloride melts at 41° and boils at 276°. The dihydrazide melts at 220°. Nitrous acid converts it into isophthalazide, C₄H₄(CON₃)₂, melting at 56°. Boiling alcohol converts it into m-phenylene-urethane, C₆H₄(NHCO₂C₂H₅)₂ (B. 29, R. 987).

m-Cyanbenzoic Acid melts at 217° (B. 20, 524). m Dicyanbenzene melts at 158° (B. 17, 1430).

Substituted Isophthalic Acids.

The 5-chlor-, 5-iod-, and 5-amidophthalic acids can be prepared from 5-nitroisophthalic acid. The nitration and sulphonation of isophthalic acid produce 5-nitroisophthalic acid and 5-sulpho-isophthalic acid (see benzoic acid, pp. 210, 216). The 4-brom-, 4-iod-, 4-amido-, and 4-sulpho-isophthalic acids are obtained by the oxidation of the corresponding toluic acids (B. 24, 3778; 28, 84; 25, 2795; 14, 2278). Tetrachlor-, tetrabrom-, and tetraiod-phthalic acids melt at 181°, 290°, and 310° (B. 29, 1632).

Homologous Isophthalic Acids.—There are four theoretically possible methyliso-

phthalic acids, of which uvitic acid may be mentioned.

Uvitic Acid, Mesidic Acid, 5 Methyl Isophthalic Acid, CH₂[5]C₆H₃[1,3](CO₂H)₂, melting at 287°, is obtained by oxidizing mesitylene with dilute nitric acid. It is formed synthetically by boiling pyroracemic acid with baryta-water (p. 42). This synthesis of uvitic acid from pyroracemic acid is due to the condensation of two molecules of pyroracemic acid with one molecule of acetaldehyde. In this reaction a portion of the pyroracemic acid is decomposed. If a mixture of pyroracemic acid and higher fatty aldehydes be used, homologous alkylisophthalic acids, C₆H₃(R)(CO₂H)₂, will result. Thus propyl aldehyde produces 5-ethylisophthalic acid, isobutyric aldehyde yields 5-isopropyl isophthalic acid, etc. (Doebner, B. 23, 377). Chromic acid oxidizes these acids to

trimesic acid (p. 245); distilled with lime, uvitic acid at first yields metatoluic acid, then

Xylidic Acid, 4-Methylisophthalic Acid, CII₃[4]C₆H₃[1,3](CO₂H)₂, melting at ≥82°, is obtained by oxidizing pseudocumene, xylic acid, and isoxylic acid with dilute mitric acid. Potassium permanganate oxidizes it to trimellitic acid.

2-Mesitylisophthalic Acid, melting at 235°, results from the reduction of 2,6-

dicarbonphenylglyoxylic acid with phosphorus and HI (B. 29, R. 283).

Oxyisophthalic Acids are obtained by the same methods from oxybenzoic acids and aldehyde oxybenzoic acids as the latter are got from phenols and phenol aldehydes. Amido- and sulphocarboxylic acids also serve as starting-out material (B. 16, 1966; 25, R. 9).

2-Oxy-, 4-Oxy-, and 5-Oxy-isophthalic Acids melt at 243°, 305°, and 288°. Oxysevitic Acids.—Mention may be made of 4-Oxyuvitic Acid, (CH3)[5](HO)[4]. C₆H₂[1,3](CO₂H)₂, produced by the action of chloroform, chloral, or trichloracetic ester upon sodium acetoacetic ester (A. 222, 249).

Terephthalic Acid, Bensene-p-dicarboxylic acid, C₆H₄[1,4](CO₂H)₂, sublimes without melting. Isophthalic acid was obtained from m-derivatives of benzene; in a similar manner terephthalic acid is formed from p-diderivatives: p-xylene, p-toluic acid, p-dicyanbenzene, p-cyanbenzoic acid, p-dibrombenzene, etc. The best course to pursue in forming terephthalic acid is to oxidize caraway oil (a mixture of cymene and cuminol) with chromic acid, or it may be prepared from p-toluidine (B. 22, 2178).

Terephthalic acid is almost perfectly insoluble in water, alcohol, and When reduced it yields di-, tetra-, and hexahydro-terephthalic ether.

acids.

The barium salt, $C_hH_4O_4Ba + 4H_2O_7$, is very sparingly soluble in water. The methyl ester melts at 140°.

The chloride melts at 78° and boils at 259°. The amic acid melts at 214°. The dihydrazide melts above 300°. The diazide, C₆H₄[1,4](CON₃)₂, melts at 110° (B. 29, R. 987).

p-Cyanbenzoic Acid, CN[4]C₂H₄CO₂H, from p-amidobenzoic acid (pp. 38, 214), melts at 214°.

p-Dicyanbenzene, C₆H₄[1,4](CN)₂, melts at 215°. Mononitroterephthalic Acid melts at 259°.

It and sulphoterephthalic acid are produced in the nitration and sulphonation of terephthalic acid. 2,3-, 2,6-, and 2,5-Dinitrophthalic Acids are also known (B. 28, 81). Consult B. 29, 1625, 2833, for tetrachlor-, tetrabrom-, and tetraiodterephthalic acids.

Alkyl Terephthalic Acids.—The oxidation of pseudocumene and durene gives rise to 4-methylterephthalic acid, a-xylidic acid, melting at 282°, and to 2,5-dimethyl-

terephthalic acid, \(\beta\)-cumidic acid (B. 19, 2510).

Oxyterephthalic Acids.—Oxyterephthalic acid has been obtained from nitroterephthalic acid. It sublimes without melting. 2,5-Dioxyterephthalic acid is the most interesting of the three possible dioxyterephthalic acids. Mention is made of it because of its connection with succino-succinic ester. Its diethyl ester may be prepared by withdrawing two hydrogen atoms from succino-succinic ester by means of bromine or PCl₅ (B. 22, 2107), or by the action of sodium ethylate upon dibromacetoacetic ester (A. 219, 78).

2,5 Dioxyterephthalic Acid, $(HO)_2C_6H_2(CO_2H)_2 + 2H_2O$, crystallizes from alcohol in yellow leaflets. Ferric chloride imparts a deep blue coloration to its solution. When rapidly distilled it decomposes into two molecules of carbon dioxide and hydroquinone.

2,5-Dioxyterephthalic Ethyl Ester crystallizes in two distinct forms: at the ordinary temperature in yellowish-green prisms or plates; at higher temperatures in colorless leastets. It also sublimes in the latter form. It melts at 133°. In most of its reactions the ester conducts itself like an hydroxyl derivative. It does not combine with hydroxylamine or phenylhydrazine, and with sodium and alkyl iodides yields dialkyl esters. It, hower, does not react with phenylcyanate (p. 89) (B. 23, 259), and shows some analogies with succino-succinic ester. Hence, it is considered a quinone- or diketo-derivative.

$$C_{\mathbf{z}}H_{\mathbf{z}}O_{\mathbf{z}}C.C < \begin{matrix} C(OH)-CH \\ CH=C(OH) \end{matrix} > C.CO_{\mathbf{z}}C_{\mathbf{z}}H_{\mathbf{z}} \text{ or } C_{\mathbf{z}}H_{\mathbf{z}}O_{\mathbf{z}}C.C < \begin{matrix} CO-CH_{\mathbf{z}} \\ CH_{\mathbf{z}}-CO \end{matrix} > C.CO_{\mathbf{z}}C_{\mathbf{z}}H_{\mathbf{z}} \end{matrix}$$

Dioxyterephthalic ester, by reduction (boiling with zinc and hydrochloric acid in alcoholic solution), is again changed to succino-succinic ester (B. 19, 432; 22, 2169). A dihydroxamic acid is formed with hydroxylamine hydrochloride; tetrahydrodioxyterephthalic acid is produced at the same time (B. 22, 1280). The different physical modifications of the ester and analogous compounds, according to Hantzsch, correspond to two desmotropic conditions—the colored variety agreeing with the quinone formula, while the colorless corresponds to the hydroxyl formula (B. 22, 1294). However, the color cannot be regarded as a certain criterion for the distinction of the ketone from the hydroxyl form. Even chemical reactions do not prove that desmotropic forms can be accepted (Nef, B. 23, R. 585; Goldschmidt, B. 23, R. 260).

Succino-succinic Acid, whose ester by the removal of hydrogen yields 2,5 dioxy terephthalic ester, will be discussed in connection with the hydro-aromatic compounds.

Trioxydicarboxylic Acids. - Gallocarboxylic Acid, Trioxy-o-phthalic Acid, (HO), [3.4.5] (1 (CO₂H)₂, melts at 270°, with decomposition. It may be prepared from pyrogallol by heating it to 130° with ammonium carbonate. Pyrogallo-carboxylic acid is formed at the same time (B. 13, 1876).

(b) Aromatic Dicarboxylic Acids containing ICO, H in the nucleus and ICO, H is the side-chain. The three a-homophthalic acids, or phenylacetic carboxylic acids, are

known. The o-acid readily forms heterocyclic derivatives.

Phenylaceto-o-carboxylic Acid, o-a-homophthalic acid, CO₃H[2]C₆H₄CH₄. CO₄H, melting at 175°, with the elimination of water, may be obtained by fusing gamloge with caustic potash (B. 19, 1654), and by saponifying cyan-o-toluic acid. Its anhydride melts at 141°.

o Homophthalimide, melting at 233°, is produced when the ammonium salt is heated, and when acids act upon the dinitrile. In the latter case o cyanphenylacetic acid, produced at first, rearranges itself into homophthalimide, just as o-cyanbenzoic acid yields phthalimide (p. 240) (B. 23, 2478). It is rather remarkable that o-homophthalimide, when heated with phosphorus oxychloride, yields dichlorisoquinoline, which becomes isoquinoline when further heated with hydriodic acid (B. 27, 2232, 2492):

$$\begin{array}{c} C_6H_4 < \begin{cases} \begin{bmatrix} 1 \end{bmatrix} CH_2CN \\ \begin{bmatrix} 2 \end{bmatrix} CN \\ \end{bmatrix} & \longrightarrow \\ C_6H_4 & \begin{bmatrix} CH_2 & CO \\ \\ CO & NH \\ \end{bmatrix} & \longrightarrow \\ C_6H_4 & \begin{bmatrix} CH & CCI \\ \\ CCI & N \\ \end{bmatrix} & \longrightarrow \\ C_6H_4 & \begin{bmatrix} CH & CCI \\ \\ \\ CH & N \\ \end{bmatrix} \\ CH & \vdots \\ CH & \vdots$$

Homophthalimide is directly converted into isoquinoline when it is heated with zinc-

The hydrogen atoms of the CH₂-groups are replaced by two alkyls when homophthalimide is heated with caustic potash and alkyl iodides. *Mono-*alkyl-o-benzylcy anides yield monoalkyl homophthalimides, which rearrange themselves in the same manner as homophthalimide into alkyl isoquinolines (B. 20, 2499).

ω Cyan o toluic Acid, CO₂H[2]C₈H₄CH₂CN, melts with decomposition at 116°. Its potassium salt is obtained from phthalide (p. 234) and potassium cyanide (A. 233,

o Cyanbenzyl Cyanide, o-a-Homophthalonitrile, CN[2]C₈H₄CH₄CN, melting at 81°, is obtained from o-cyanbenzyl chloride (p. 234). Caustic potash and alkylogens effect the replacement of an hydrogen atom in the methylene group by an alcohol radical (see homophthalimide). Acetyl chloride converts it into \(\psi\)-diacetyl-o-cyanbenzyl cyanide, CN. C₆H₄C(CN): C(CH₃)OCOCH₃, which may be rearranged into 3-methylisoquinoline (B. 27, 2232).

Homoisophthalic Acid and homoterephthalic acid melt at 237°. Both sublime. m and p Cyanbenzyl Cyanides melt at 88° and 100° (B. 24, 2416). The dimitrile, the two nitrilo- and amic acids, the two possible amido-nitriles, and the diamide of homo-

terephthalic acid have been prepared (B. 22, 3207; 26, R. 89, 602).

o-Hydrocinnamic Carboxylic Acid, CO₂H[2]C₆H₄CH₂CH₂CO₂H, melts at 165°.

It is formed by oxidizing tetrahydro-β-naphthylamine with potassium permanganate, and by the reduction of dibydroisocoumarine carboxylic acid (B. 26, 1841), as well as from o-carbonphenyl glyceric acid-o-lactone (B. 25, 888). It yields a hydrindone (B. 26, 708) upon dry distillation.

o-Cyanbenzyl Acetic Ester, Cyanhydrocinnamic Ester, CN[2]C₆H₄[1]-CH₄. CH₂. CO₂C₂H₅, melting at 98°, is produced by the rearrangement of the product resulting from the action of acetoacetic ester or malonic ester and sodium ethylate upon cyanbenzyl chloride (B. 22, 2017). Concentrated hydrochloric acid converts it into a-hydrindone (see this): $C_6H_4 < {}_{CO}^{CH_2} > CH_2$.

Phenylbutyric-o-carboxylic Acid, CO₂H[2]C₆H₄CH₂. CH₂. CH₂. CO₂H, melts

at 138° (B. 18, 3118).

(c) Aromatic Dicarboxylic Acids, having both carboxyls in different side-groups.
o., m., and p.Phenylene Diacetic Acids, C.H. (CH.CO.H.), melting at 150°, 170°, and 244°, have been obtained from the xylylene cyanides (B. 26, R. 941).

o-Phenylene diacetic acid has also been prepared by oxidizing dihydronaphthalene (see

this). Its calcium salt yields β-hydrindone upon distillation (see this) (B. 26, 1833).
o-Phenyleneaceto-propionic Acid, C₄H₄(CH₂. COOH)[2](CH₂. CH₂COOH), melting at 139°, is obtained from β-oxy-a-naphthoic acid by rupture of the ring, effected by sodium and amyl alcohol, just as pimelic acid is formed from salicylic acid (pp. 47, 222). It reverts to β -ketotetrahydronaphthalene when its calcium salt is distilled (B. 28, R. 745).

o-, m-, and p-Phenylene Dipropionic Acids, CaH4(CH2. CH2. CO3H), melting at 161°, 146°, and 223°, are formed from xylylene dimalonic acids (B. 19, 436; 21, 37).

9. ALDEHYDO-DICARBOXYLIC ACIDS.

2-Aldehydo-isophthalic Acid, melting at 175° to 176°, results from heating 2,6-di-

carbophenylglyoxylic acid (B. 26, 1767; 30, 695).

5-Aldehydo-4-oxy- and 5-aldehydo-3-oxyisophthalic acids are formed from the corresponding oxyisophthalic acids by means of chloroform and caustic potash (B. 11, 793).

10. TRICARBOXYLIC ACIDS.

The three isomeric benzene tricarboxylic acids, C₆H₃(CO₂H)₃, are known. Trimesic Acid, (1,3,5) Benzenetricarboxylic Acid, melts about 300°, and sublimes near 200°. It is formed (1) when mesitylenic and uvitic acids are oxidized with a chromic acid mixture; (2) by heating mellitic acid with glycerol, or hydro- and isohydromellitic acid with sulphuric acid. A synthetic method for its production consists in (3) heating benzene-1,3,5 trisulphonic acid with potassium cyanide and saponifying the resulting cyanide. By the condensation of certain aliphatic substances the acid and its esters have been obtained (1) by polymerizing propiolic acid; (2) by the production of its monomethyl ester through the action of caustic potash upon coumalic acid (B. 24, R. 750); (3) its triethyl ester from formyl acetic ester. Its trimethyl ester melts at 143°. Its triethyl ester melts at 133°.

Trimellitic Acid, (1,2,4). Bensene tricarboxylic Acid. This is obtained (together with isophthalic acid) by heating hydropyro-mellitic acid with sulphuric acid, or upon This is obtained (together oxidizing xylidic acid with potassium permanganate, also from amidoterephthalic acid (B. 19, 1635). It is prepared most readily (along with isophthalic acid) by oxidizing colophony with nitric acid (A. 172, 97). It melts at 216°, decomposing into water and the anhydride, C₈H₂(CO₂H)(CO)₂O. The latter melts at 158°.

Hemimellitic Acid, (1,2,3). Benzene tricarboxylic Acid. This is formed on heating

bydromellophanic acid (below) with sulphuric acid, as well as in the oxidation of phenyl-

glyoxyldicarboxylic acid, formed from naphthalic acid by action of KMnO₄ (B. 29, 283). It melts at 185° and decomposes into phthalic anhydride.

Oxytricarboxylic Acids have been obtained from the sulphotricarboxylic acids:

oxytrimesic acid (A. 206, 204); oxytrimellitic acid—see B. 16, 192.

Phloroglucin-tricarboxylic ester and dloxyphenylaceto-dicarboxylic ester, ondensation products of sodium malonic ester and sodium acetone dicarboxylic ester, are probably hydroaromatic compounds.

11. AROMATIC TETRACARBOXYLIC ACIDS.

The three isomerides are known. Reduction converts them into tetrahydrobenzene

tetracarboxylic acids (see these).

Pyromellitic Acid, 1,2,4,5. Benzene Tetracarboxylic Acid, $C_8H_2(CO_2H)_4 + 2H_2O_1$ melts when anhydrous at 264° and decomposes into water and its anhydride, which is produced when mellitic acid is distilled, or, better, when the sodium salt is subjected to the same treatment with sulphuric acid. The acid is also produced by oxidizing durene and durylic acid with potassium permanganate.

The dianhydride, C₆H₁(CO CO)₂, melts at 286°. The ethyl ester, C₆H₂(CO₁.

 $C_2 H_5$)₄, melts at 53°.

Dinitro- and diamidohydromellitic tetraethyl esters melt at 130° and 134°.

Nitric acid oxidizes the diamido-ether to:

Quinone Tetracarboxylic Ester, $C_6(O_2)(CO_2, C_2H_6)_4$, crystallizing in quinone-yellow needles, melting at 149°. It is odorless, but sublimes quite readily. Zinc reduces it in glacial acetic acid solution to—

Hydroquinone Tetracarboxylic Ester, $C_8(OH)_2(CO_2 \cdot C_2H_5)_4$, crystallizing in bright yellow needles, melting at 127°. In alcoholic solution it is reduced by zinc-dust and hydrochloric solid to p-diketohexamethylene-tetracarboxylic ester (A. 227, 25).

and hydrochloric acid to p-diketohexamethylene-tetracarboxylic ester (A. 237, 25).

Prehnitic Acid, (1,2,3,4)-benzene tetracarboxylic acid, C₆H₂(CO₂H)₄ + 2H₂O, melts when anhydrous at 237°, with the formation of an anhydride. It results (together with mellophanic acid and trimesic acid) upon heating hydro- and isohydro-mellitic acid with sulphuric acid, also by oxidizing prehnitol with potassium permanganate (B. 21, 907).

Mellophanic Acid (1,2,3,5)-benzene tetracarboxylic acid, melts at 238°, with anhydride formation. It is formed by the oxidation of isodurene with KMnO₄; see prehnitic

acid.

12. AROMATIC PENTACARBOXYLIC ACID.

Benzene Pentacarboxylic Acid, $C_6H(CO_2H)_5+6H_2O$, decomposes when it is melted. It is produced by oxidizing penta-methylbenzene with permanganate (B. 17, R. 376).

13. AROMATIC HEXACARBOXYLIC ACID.

Mellitic Acid, C₆(CO₂H)₆. When heated it melts and decomposes into water, carbon dioxide, and pyromellitic anhydride.

Honey-stone, found in some lignite beds, is an aluminium salt of mellitic acid, crystallizing in large quadratic pyramids of bright yellow color (B.

10, 566).

An interesting formation of mellitic acid is that whereby pure carbon (graphite, charcoal, etc.) is oxidized with an alkaline solution of potassium permanganate. Another is when the carbon is applied as positive electrode in electrolysis (B. 16, 1209), and also the oxidation of hexamethyl benzene with KMnO₄.

As hexamethyl benzene can be synthesized, this latter method of formation would be a synthesis of mellitic acid.

Mellitic acid crystallizes in fine, silky needles, readily soluble in water and alcohol. It is very stable, and is not decomposed by acids, by chlorine, or bromine, even upon boiling. It yields benzene when distilled with lime.

History.—Klaproth (1799) discovered mellitic acid by boiling honey-stone for a long period with water, and named it honey-stone acid. In 1870 Baeyer proved that mellitic acid was nothing more than benzene hexacarboxylic acid, in that by heating with lime he obtained benzene and by reduction found hexahydromellitic acid (A. suppl., 7, 1).

Salts and Esters.—The barium salt, C₁₂Ba₂O₁₂ + 3H₂O, is insoluble in water. The methyl ester melts at 187°; the ethyl ester melts at 73°.

The chloride, C₆(COCl)₆, melts at 190°.

Mellimide, Paramide, C₆ (CO) NH)₂, is formed in the dry distillation of the ammonium salt. It is a white, amorphous powder, insoluble in water and alcohol. Heated to 200° with water, it is converted into the tri-ammonium salt of mellitic acid. The alkalies convert paramide into euchroic acid.

Euchroic Acid, C₆[(CO)₂NH]₂ {CO.OH, crystallizes in colorless prisms. Heated with water to 200°, it yields mellitic acid. Nascent hydrogen changes euchroic acid to euchrone, a dark blue precipitate, which reverts to colorless euchroic acid upon exposure. Euchrone dissolves with a dark red color in alkalies.

3. AROMATIC POLYALCOHOLS, CONTAINING MORE THAN ONE HYDROXYL GROUP IN THE SAME SIDE-CHAIN, AND THEIR OXIDATION PRODUCTS.

Of the aromatic polyalcohols, having the hydroxyl groups attached to different carbon atoms of the same side-chain, it is only the glycols and their oxidation products which have been studied in any sense completely. A more detailed classification of the polyhydric alcohols and their oxidation products is therefore unnecessary; the compounds belonging here will, for practical considerations, be included with the glycols and their oxidation products.

The methods of formation as they were applied in the preparation of aliphatic glycols and their oxidation products (1, 289) are more extensively and fully used for the phenyl glycols and their oxidation products than they have been in connection with any of the previously discussed aromatic derivatives.

1. PHENYL GLYCOLS AND PHENYL GLYCEROL.

Styrolene Alcohol, C_6H_5 . CH(OH). CH₂. OH, *Phenyl glycol*, melts at 67°, boils at 273°, and is obtained from styrolene dibromide by the action of a potash solution. Dilute nitric acid oxidizes it to benzoyl carbinol and benzoyl formic acid (A. 216, 293). Two molecules are condensed by dilute sulphuric acid to β -phenyl naphthalene (see this). Styrolene Dichloride, a,β -dichlorethyl benzene, C_6H_5 CHCl. CH₂Cl, is liquid, while the dibromide melts at 60°. They result from the addition of halogens to styrene (see this) or phenylethylene.

Phenyl Methyl Glycol, C₈H₅. CH(OH). CH(OH). CH₃, exists in two modifica-

tions, a and β, like hydrobenzoln. These are obtained from phenyl dibrompapese (from n-propyl benzene). The a-body melts at 53°, the β- at 93° (B. 17, 709). Phenyl Butylene Glycol, C₆H₆CH(OH)CH₂. CH₂. CH₂(OH), melting at 75°, is obtained by reduction from benzoylpropionic aldehyde (p. 250) and benzoylpropyl

alcohol.

Phenylisopropyl Ethylene Glycol, CaHaCH(OH)CH(OH)CH(CHa), meking at 81° and boiling at 286°, results from the reduction of benzaldehyde and isobutylakie

hyde.

Methylene m,p-dioxybenzyl Glycol, [CH₂O₂][3,4]C₂H₂CH₂CH(OH)CH₂(OH), melting at 82°, and Methylene-m.p.dioxyphenylethylenemethyl Glycol, (CHQ)-[3,4]C,H₂, CH(OH). CH(OH). CH₃, melting at 101°, result from the action of Klaso (1: 24, 3488) upon safrol and isosafrol. The corresponding glycols, melting at 68° and

88°, are obtained from engenol and isoengenol (see these).

Stycerine, C₆H₆. CH(OH). CH(OH). CH₂. OH, a gummy mass, is obtained from styrone bromide and cinnamic alcohol, C₆H₆. CHBr. CHBr. CH₂. OH, with potsssins

permanganate (B. 24, 3491).

2. PHENYLALCOHOL ALDEHYDES.

Just as two molecules of acetaldehyde condense to aldol, so the nitrobenzaldehydes combine with acetaldehyde, under the influence of very dilute sodium hydroxide (2 per cent.) to the corresponding aldols, the nitrophenyl-lactic acid aldehydes, NO₂C₄H₄-('H(OH)CH2CHO, which unite with an additional molecule of acetaldehyde. Dehydrating agents, like acetic anhydride, convert them into the corresponding nitrotin-

namic aldehydes (B. 18, 719).

Phenyltetrose, C₆H₅. CII(OH)CH. OH. CH(OH). COH, is a colorless symp resulting from the reduction of phenyltrioxybutyric acid lactone (see this). Its phenyl-

hydrazone melts at 154°.

3. PHENYL KETOLS.

Acetophenone Alcohol, Benzoyl Carbinol, CoH6. CO. CH2. OH, crystallizes from water and dilute alcohol in large, brilliant leaflets, which contain water of crystallization, and melt at 73-74°. It crystallizes from ether in shining anhydrous plates, and melts at 85°. It is produced in the oxidation of phenyl glycol, and from its chloride, \(\omega\)-chloracetophenone, by its conversion into acetate and saponification with potassium carbonate (B. 16, 1290).

When distilled it decomposes, with formation of bitter-almond oil. Being a ketone, it forms crystalline compounds with primary alkaline sulphites. Like acetyl carbinol, it reduces a cold ammoniacal silver or copper solution (forming benzaldehyde and benzoic acid), and is oxidized to mandelic acid (p. 251) (B. 14, 2100). Nitric acid oxidizes it to phenylglyoxylic acid. It yields cyanhydrin with CNH, which then forms a phenylglyc-

eric acid, or atroglyceric acid (see this).

 $C_6H_5C(O.CH_3)$ —O— CH_2 Bismethylbenzoyl Carbinol,

сн.-O-C(OCH₃)C₆H₅ (?), melting at 192°, is formed from benzoyl carbinol with methyl alcohol and hydrochloric acid (B. 28,

Benzoyl Carbinol Acetate, C₆H₅CO. CH₂. O. COCH₃, melts at 49° and boils at 270°. The benzoale melts at 117°. The phenyl-ether melts at 72°.

ω-Chloracetophenone, Phenacyl Chloride, Benzoyl Carbinol Chloride, CaHoCO-CH₂Cl, melting at 59° and boiling at 245°, results from the chloring and aluminium phenone (B. 10, 1830), as well as from benzene, chloracetyl chloride, and aluminium

ω Bromacetophenone, C_eH₆. CO. CH₂Br, melting at 50°, attacks the mucous membrane quite powerfully. It is obtained from acetophenone and bromine, also by heating dibromateologician heating distromatrolactinic acid with water (B. 14, 1238). An excess of alcoholic ammonia changes it to isoindol—a hydrazine derivative. The acid amides and thismides change the a-haloid section. change the & haloid acetophenones into oxazole and thiazole derivatives (see these).

Gallo-chlor-acetophenone, $C_aH_2(OH)_2COCH_2Cl$, and ω -bromresacetophenone, containing the hydroxyl group in the ortho-position, part with halogen hydrides, and become ketocumaran- or ketodihydrocumarone derivatives (B. 30, 299).

ω-Amidoacetophenone, C₂H₅. CO. CH₂. NH₃, is very unstable in a free condition. Separated from its hydrochloride by means of sodium hydroxide, it changes to the base $C_{16}H_{14}N_2O$, melting at 118°, which yields isoindol in the presence of ammonia. The hydrochloride, C_4H_5 . CO. CH₂. NH₂HCl, melting at 183°, is formed when the isonitrosoacetophenone is reduced with tin and hydrochloric acid (B. 28, 254). For the action of nitrous acid upon the hydrochloride see B. 26, 1717; 29, R. 298. Potassium cyanate (B. 28, 252) produces phenylacetylene monourein, or phenylimidazolon (see this). ω Acetophenone-anilide, ohenacyl anilide, $C_6\Pi_5$. CO. CH₅. NHC₆H₅, melting at 93°, is formed from ω -bromacetophenone and aniline (B. 15, 2467), and may be condensed to a-phenylindol (B. 21, 1071, 2196, 2595).

Benzoylcarbinoloxime melts at 70°. The phenylhydrasone, melting at 112°, is con-

verted by phenylhydrazine into an osazone of phenylglyoxal (B. 20, 822).
o- and m-Nitro-ω-bromacetophenones melt at 55° and 96° (A. 221, 327).
a-Amidopropiophenone, C₆H₅. CO. CHNH₄. CH₃ (B. 22, 3250).

Corresponding to the nitrophenyllactic acid aldehydes we have o- and p-Nitrophenyllactic acid ketones, melting at 69° and 58°; these are the condensation products of o- and p-nitrobenzaldehyde and acetone in the presence of very dilute sodium hydroxide. Boiling water or an excess of sodium hydrate causes the o-nitroketone to give up acetic acid and water, changing thereby into indigo (B. 16, 1968). See the nitrobenzylidene acetones.

Benzoylbutylcarbinol, C₂H₆. CO. [CH₂]₃. CH₂OII, melts at 40° (B. 23, R.

4. PHENYLALDEHYDE KETONES.

a-Ketone Aldehydes.—Phenyl Glyoxal, Benzoyl formaldehyde, CeH5. CO. CH(OH), melts at 73°. The anhydrous aldehyde boils at 142° (125 mm.). It has a penetrating odor. It is obtained from its aldoxime, isonitrosoacetophenone, upon boiling the sodium sulphite derivative with dilute sulphuric acid (B. 22, 2557). Alkalies convert it into mandelic acid (p. 251); potassium cyanide condenses it to benzoylformoin, just as it

manuenc acid (p. 251); potassium cyanide condenses it to benzoylformoin, just as it changes benzaldehyde to benzoin. It yields quinoxalines with o-diamines.

• Dichloracetophenone, C₈H₅. CO. CHCl₂, boils at 253° (B. 10, 531). • Dibromacetophenone, C₈H₅. CO. CHBr₂, melts at 36° (B. 10, 2010; A. 195, 161).

• Dibrom-p-iodacetophenone (B. 24, 997). • Dichlor-o-nitroacetophenone melts at 73° (A. 221, 328). • Dibrom-o-, -m-, and p-nitroacetophenones melt at 85° 50° and 88° (B. 20 2022; 18 2020; 28 2020).

85°, 59°, and 98° (B. 20, 2203; 18, 2240; 22, 204).

Isonitrosoacetophenone, Benzoylformoxime, C₄H₆CO.CH(N.OH), melting at 127°, is obtained from acetophenone (p. 189) (B. 24, 1382; 25, 3459). It forms isoindol (p. 248) by reduction. Phenyl Glyoxime, C₆H₅C(NOH). CH(NOH), is known in two modifications (compare benzildioximes):

$$\begin{array}{ccccc} C_6H_5 \cdot C - & C \cdot H & C_6H_5C - CH \\ \parallel & \parallel & (?) \\ N \cdot OH & N \cdot OH & HO \cdot N & N \cdot OH \\ \end{array}$$

$$\begin{array}{ccccc} Phenylamphiglyoxime & Phenylantiglyoxime (melts at 186°). \end{array}$$

Phenylamphiglyoxime is produced when hydroxylamine acts upon ω -dibromacetophenone and isonitrosoacetophenone. When treated in absolute ether with hydrochloric acid gas, it changes to the anti-modification, which reverts to the amphi-modification by recrystallization from indifferent solvents (B. 24, 3497).

a- and β -Phenylglyoxalphenylhydrazones melt at 142° and 129° (B. 22, 2557). Phenylglyoxalphenylosazone, C_6H_5 . C: (N. NH. C_6H_5). CH: (N. NH C_6H_5), melts at 152°. (See benzoylcarbinolphenylhydrazone) (B. 22, 2558). Phenylglyoxalmethylphenylosazone melts at 152° (B. 21, 2597).
p-Toluic formaldehyde, CH₂C₂H₄CO. CH(OH)₃, melts at 101° (B. 22, 2560).

Anthroxanaldehyde, C₆H₄ { [z] C—CHO [2] N>O , melting at 72°, is formed from o-airo-

phenylglycidic acid (p. 256) (B. 16, 2222) (compare anthranil, p. 212).

B. Keton-aldehydes. - Formylacetophenone, or benzoylacetaldehyde, was formerly regarded as B-keton-aldehyde, in which, as in formylacetone, an unsaturated ketol, oxymethylese acetophenone, is present. This will, therefore, be discussed later in connection with the compounds containing an unsaturated side chain. The sodium salt of oxymethylese acetophenone and hydroxylamine hydrochloride yield benzoylacetaldozime, C.H... C(). CH₂. CH: N. ()H, melting at 86°, which acetic anhydride converts into cyanacto-phenone (p. 260), and acetyl chloride into the isomeric phenylisoxazole.

y- Keton-aldehydes.—Benzoylpropionaldehyde, CaHaCO. CHa. CHa. CHa, bolk at

245°.

5. PHENYL PARAFFIN DIKETONES.

a-Diketones, or orthodiketones, are produced from their monoximes, the phenylisonitrosoketones (compare phenylglyoxal) by distillation with dilute acids (1, 326), or by digesting with amyl nitrite (B. 21, 2177). Benzoyl Acetyl, CaH₆. CO.CO.CH, lkoiling at 214°, is a yellow oil with a peculiar odor (B. 21, 2119, 2176).

a. Oximidopropiophenone, CaH₈, CO, C: (NOH). CH₈, melting at 113°, results

from the action of nitrous acid upon methylbenzoylacetic ester.

Di-isonitrosoanethol Peroxide, CH₃O[4]C₆H₄ . C ____c. сн<u>.,</u> melting at 97°, results from the action of sodium nitrite upon anethol in glacial acetic acid solution (R. 26, R. 891).

The B. or meta diketones result, together with acetophenone, (1) from the decomposition of the benzoylacetoacetic esters (B. 16, 2239); further, by (2) a remarkable

condensation induced by sodium alcoholate (Claisen, B. 20, 2178).

The β diketones behave like the β -diketones of the fatty series. They dissolve in alkalies. This distinguishes them from the other diketones. They are colored an intense red by ferric chloride. They condense to isoxazoles with hydroxylamine (B. 21, 1150). They form pyrazole compounds with phenylhydrazine, just like the oxymethylene-3-ketones.

Benzoyl Acetone, acetyl acetophenone, CoH3. CO. CH3. melts at 60-61°, boils at 260-262°, and readily volatilizes with steam. It is formed from benzoylacctoacetic ester, from ethyl benzoate and acctone or ethyl acctate and acctophenone with sodium ethylate, free from alcohol. See B. 27, 1571, for the addition of CNH to benzoyl acctone. See J. pr. Ch. [2] 48, 489, for the action of urea and guanidine. o-Nitro-benzoyl Acctone melts at 55° (A. 221, 332).

Propionyl-, butyryl-, isobutyryl-, and valerylacetophenones boil at 172° (30 mm.), 174° (24 mm.), 170° (26 mm.), and 183° (30 mm.) (B. 20, 2181). Phenyl-acetyl-acetone, $C_{11}H_{12}O_2=C_6H_5$. CH_2 . CO. CH_3 . boiling at 266°, results from the decomposition of phenyl acetyl-acetoacetic ester (B. 18, 2137).

The following is a y-diketone:

Acetophenone-acetone, phenacylacetone, CaH5. CO. CH2. CH2. CO. CH3, is obtained from acetophenone acetoacetic ester. It is a yellow oil, boiling with decomposition (B. 17, 2756).

Being a y-diketone, it can split off water and yield phenylmethylfurfurane, phenyl-

methylthiophene, and phenylmethyl pyrrol.

Triketones.—Isonitrosobenzoyl Acetone, Call CO. C(NOH). CO. CH, melting at 24°, is the monoxime of a triketone (B. 17, 815).

6. PHENYL PARAFFIN ALCOHOL ACIDS.

A. Monoxyalcohol Acids.—Phenylalcohol carboxylic acids, like the aliphatic alcohol acids, are produced (1) by the reduction of the corresponding ketonic acids; (2) from aldehydes and ketones (B. 12

8 15) by the addition of hydrocyanic acid and the saponification of the **2-oxy-acid nitrile**; (3) from the corresponding monohalogen acids; (4) from unsaturated monocarboxylic acids, etc.

e-and β-Oxy-acids.—Mandelic Acid, Phenylglycollic Acid,

C.H. CHOH. CO.H, is isomeric with the cresotinic acids (p. 225) and the oxymethylbenzoic acids (p. 234) or carbinol benzoic acids. It contains an asymmetric carbon atom, and therefore, like lactic acid of fermentation (1, 335), appears in one inactive, decomposable and two Optically active modifications.

Paramandelic Acid, inactive mandelic acid, melting at 118°, is formed (1) from benzaldehyde, prussic acid, and hydrochloric acid (B. 14, 239, 1965); (2) from benzoylformic acid (p. 257), by reduction with sodium amalgam; and (3) from phenylchloracetic acid by boiling it with alkalies (B. 14, 239), (4) as well as from ω -dibromacetophenone (p. 249) or phenyl glyoxal (p. 249) by the action of alkalies: C.H. CO. $CHO \longrightarrow C_{\bullet}H_{\bullet}$. CHOH. CO, H.

The production of alcohol and carboxylic acid, which completes itself extramolecularly in the action of caustic alkali upon benzaldehyde, in the case of the conversion of phenyl glyoxal into mandelic acid proceeds intramolecularly (1, 321). See further on for the formation of paramandelic acid from levo- and dextromandelic acids.

One hundred parts water at 20° dissolve 15.9 parts of paramandelic acid. Dilute nitric acid converts it first into benzoyl-formic acid, then into benzoic acid. When heated with hydriodic acid it forms phenyl-acetic acid; with hydrobromic and hydro-

chloric acids, chlorphenyl or bromphenyl acetic acids.

Levo- and dextromandelic Acids melt at 133°. They have equal, but of molecular rotatory power. Toward reagents they behave like paramandelic acid. They have equal, but opposite, mandelic acid, natural mandelic acid, results upon digesting amygdalin (see this) with fuming hydrochloric acid (1848-Wöhler, A. 66, 240). Fermentation of ammonium paramandelate with Penicillium glaucum destroys the lavo- and there remains the dextro-acid. Schizomycetes first destroys the dextro-mandelic acid in paramandelic acid; the lævo-acid remains (Lewkowitsch, B. 17, 2723). The direct splitting up of paramandelic acid into the dextro- and lævo-acids can be brought about by the crystallization of the cinchonine salt. The mixing together of the dextro- and lævo-acids (molecular quantities) results in the formation of inactive paramandelic acid. When the dextro- or levo-acid is heated in a tube to 160°, it is converted into the inactive mandelic acid.

Derivatives of Paramandelic Acid.—The methyl and ethyl esters melt at 52° and 34° (B. 28, 259). The methyl ether-acid melts at 71°. The dimethyl ether-acid boils at 246° (A. 220, 40). Acetyl Ethyl Ester melts at 74°. Mandelic Chloralide (1, 340) melts at 82° (A. 193, 40). The amide melts at 131° (B. 25, 2212).

Mandelic Acid Nitrile, C₈H₅. CHOH. CN, is a colorless oil, solidifying at —10°. At 170° it breaks down into prussic acid and benzaldehyde. On standing with fuming hydrochloric acid it passes into the amide; and, when heated, into phenylchloracetic cid (B. 24, 1667). It condenses with heaveldehyde to disharulospeed (B. 20, 207). acid (B. 14, 1967). It condenses with benzaldehyde to diphenyloxasole (B. 29, 207; R. 791).

p-Brom- and p-iod-mandelic acids melt at 117° and 133° (B. 24, 997; 23, 3467). o-, m-, and p-Nitromandelic Acids melt at 140°, 119°, and 126° (B. 20,

2203; 22, 208).

o-Amido-mandelic Acid, Hydrindic Acid, NH₂[2]C₆H₄CH(OH)CO₂H, is not stable in a free condition. Its sodium salt, C₈H₈NO₃Na + H₂O₃ is formed in the reduction of isatin with sodium amalgam. From concentrated solutions of the sodium salt acids separate

produced when isatin and zinc-dust, water, and some hydrochloric acid are boiled. Acetyldioxindol, melting at 127°, is converted by baryta-water into o-acetamido-mandelic acid, CH₃CONH[2]C₄H₄CH(OH)CO₂H, melting at 142°, which also result from the reduction of acetylisatinic acid. Hydriodic acid or sodium amalgam changes it to oxindol (p. 224).

p. Dimethylamidophenyl-trichlorethyl alcohol (p. 187) is a derivative of p-amido-

mandelic acid.

o-Oxymandelic Acid, obtained from salicylaldebyde, prussic acid, and also from o-oxyphenyl glyoxylic acid, is a syrupy mass. Its lactone melts at 40° and boils at 237° (B. 14, 1317; 17, 974). p-Methoxymandelic Acid, from anisaldehyde, melts at 93° (B. 14, 1976).

Phenylchloracetic Acid, C₆II₅. CHCl. CO₂H, melting at 78°, is produced when mandelic acid is heated with concentrated hydrochloric acid to 140°, and by action of water upon its chloride. Its chloride, C₆H₅. CHCl. COCl, formed by the action of P('l₅ upon mandelic acid, boils at 125° (45 mm.) (A. 279, 122). Phenylbromacetic Acid, C₆H₅. CHBrCO₂H, melts at 83°. Its chlyl ester, boiling at 145° (10 mm.) (B. 24, 1877), when heated with potassium cyanide becomes diphenyl-specials enter. Its mitric from heavyl cyanide and heaving when heated store here succinic ester. Its nitrile, from benzyl cyanide and bromine, when heated alone becomes stilbene; when heated with potassium cyanide it yields stilbene or dicyandibeary (see this); while with alcoholic potash, stilbene dicarboxylic acid or diphenyl malek acid is produced.

Phenylamido-acetic Acid, C₆H₆. CH(NH₂). CO₂H, melts at 256°. It yields CO₂ and benzylamine when it is distilled. It results (1) on treating phenylbromacetic acid with aqueous ammonia (B. 11, 2002); (2) on boiling its nitrile with dilute sulphnic acid (II. 13, 383), and (3) by the reduction of its oxime or the phenylhydrazose of benzoyl formic acid (A. 227, 344). Its methyl ester melts at 32°. Cyclic Double-acid Amide (I, 357), C₆II₅. CII < CO-NH > CH . C₆H₅, melts with decomposition at 274°

(B. 24, 4149). Its nitrile is a yellow oil, which gradually solidifies to a crystalline mass. It is very decomposable. It results from the action of ammonia upon mandelic nitrile.

Alkylic and phenylated phenylamido-acetic acids are obtained as the result of the action of methylamine, aniline, and similar bases upon phenylbrom-acetic acid (B. 15,

Of the alphylglycollic acids, mention may yet be made of p-Isopropyl-mandelic Acid, prepared from cumic aldehyde, prussic acid, and hydrochloric acid. It, too, has been resolved by means of quinine into its active isomerides (B. 26, R. 89).

Phenyloxypropionic Acids, Phenyl-lactic Acids.—There are four possible structural isomerides. All are known and contain an asymmetric carbon atom:

I. Atrolactinic Acid, a Phenyl·lactic Acid, C₂H₁₀O₃ + 1½H₂O, melts when in the hydrous state at 90°, and when anhydrous at 94°. It is obtained from a bromhydroatropic acid when the latter is boiled with a soda solution, and by oxidizing hydroatropic acid with potassium permanganate. It is prepared synthetically from acetophenone, C₈H₅, CO, CH₅, by means of prussic acid and sulphuric acid or dilute hydrochloric acid (B. 14, 1980). When boiled with concentrated hydrochloric acid it decomposes into water and atropic acid.

Corresponding to atrolactinic acid are a-chlor- and a-bromhydratropic acids, melting at 73° and 93°, which are produced when it stands in contact with concentrated haloid acids (A. 209, 3). a-Amidohydratropic Acid sublimes, without melting, at

260° (B. 14, 1981).
2. Tropic Acid, a-Phenylhydracrylic Acid, is known in an inactive, decomposable

Inactive tropic acid, melting at 117°, is obtained, together with tropine (see this) (A. 138, 233; B. 13, 254), on digesting (60°) the alkaloids atropine and hyoscyamine with baryta-water. It was made synthetically from atropic acid, the decomposition product of atrolactinic acid, by changing it with concentrated hydrochloric acid into β-chlorhydratropic acid, which boiling potassium carbonate converts into inactive tropic

Levo- and dextro-tropic acids, melting at 128° and 123°, can be separated by the fractional crystallization of their quinine salts. The dextro-quinine salt, more sparingly soluble in dilute alcohol, melts at 186°, and the lævo-salt at 178° (B. 22, 2591).

 β -Chlor- and β -Bromhydratropic Acids melt at 87° and 93°.

 β-Amidohydratropic Acid melts at 119° (A. 209, 3).
 β-Phenyl-lactic Acid, Bensylglycollic acid, C₆H₅. CH₂. CH. (OH). CO₂H₃. melting at 97°, is derived from phenylacetaldehyde with prussic acid and hydrochloric acid, and from benzyltartronic acid upon heating it to 180°. IIeated with dilute sulphuric acid, it decomposes into phenylacetaldehyde and formic acid.

Phenylalanine, β-Phenyl-a-amidopropionic Acid, C₆H₆. CII₂. CH(NII₂). CO₂H₇, sublimes without decomposition when it is slowly heated. Upon rapid heating it yields

phenylethylamine and a cyclic double-acid amide,

C₆H₅. CH₂. CH. < CO. NH CO. CH. CH₂. C₆H₅, melting at 290° (1, 357; 11, 252) (A. 219, 188; 271, 169). It is found, along with asparagine (1, 490), in the sprouts of Lupinus luteus, and is formed in the decay or by the chemical decomposition of albumen (B. 16, 1711). It is prepared from its nitrile, the product of the action of ammonia upon the nitrile of β -phenyllactic acid, with hydrochloric acid; further, by the reduction of a amidocinnamic acid (B. 17, 1623), and of a isonitroso β -phenylpropionic acid (A. 271, 169). Benzoyl Phenyl-alanine, from benzoylamidocinnamic acid by reduction, melts at 182° (A. 275, 15).

o- and p-Nitrophenyl-lactic Acids are produced in the nitration of phenyltic acid. When reduced the o-acid yields oxyhydrocarbostyril (pp. 214, 255), lactic acid. $[I]CH_{\bullet}$ —CH.OH

C₈H₄ {[2]NH—CO , melting at 197°, and the p-aciu, p-aintide-p-production at 188°.

acid, NH₂[4]C₈H₄. CH₃. CH(OH)CO₂H, melting with decomposition at 188°.

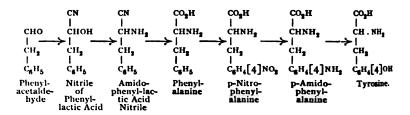
o-Oxyphenyl-lactic Acid, Salicyl-lactic acid, HO[2]C₈H₄CH₂CH(OH)CO₃H, is a racemic acid (p. 259) (B. 18, 1188). Its inner phenol alcohol-anhydride is hydrocoumarilic acid, C₈H₄ { [1]CH₂. CH. CO₂H, melting at 118°. This is the reduction syrup-like mass. It results from the action of sodium amalgam upon o-oxyphenyl pyroproduct of coumarilic acid (A. 216, 166). p-Oxyphenyl-lactic Acid melts at 144° in the anhydrous condition. It is formed when an excess of nitrous acid acts upon p-amidophenylalanine (A. 219, 226).
p. Nitrophenylalanine, NO₂[4]C₆H₄CH₂. CH(NH₂)CO₂H, decomposes at 240°.

It is formed in the nitration of phenylalanine.
p-Amidophenylalanine, NH₂[4]C₂H₄. CH₂. CH(NH₂). CO₂H, is produced in the reduction of p-nitrophenylalanine and p-nitrophenyl-a-nitroacrylic acid.

Tyrosine, p-Oxyphenyl-alanine, HO[4]C₆H₄. CH₂CH(NH₂)CO₂H, melts at 235°. It occurs in the liver when its functions are disturbed, the spleen, the pancreas, and in stale cheese (τυρός), and is formed from animal substances (urea, horn, hair, albumen) on boiling them with hydrochloric or sulphuric acid; by fusion with alkalies or by putrefaction (together with leucine, aspartic acid, etc.). It may be prepared synthetically from p-amidophenylalanine by the action of one molecule of potassium nitrite upon the hydrochloric acid salt.

History.—Liebig discovered tyrosine upon fusing freshly prepared cheese with causic potash (1846) (A. 57, 127; 62, 269). E. Erlenmeyer, Sr., and Lipp (A. 219, 161) succeeded in synthesizing tyrosine, beginning with phenylacetaldehyde.

Synthesis of Tyrosine.—Phenylacetaldehyde (p. 189) and prussic acid yield the nitrile of phenyl-lactic acid. Ammonia changes the latter to the nitrile of phenylalanine, which hydrochloric acid converts into phenylalanine. The latter by nitration yields p-nitrophenylalanine, whose reduction product, p-amidophenylalanine hydrochloride, is changed by an equimolecular quantity of nitrous acid into tyrosine:



Properties and Department.—It dissolves in 150 parts of boiling water, and crystallizes in delicate, silky needles. It dissolves in alcohol with difficulty, and is insoluble in ether.

Mercuric nitrate produces a yellow precipitate, which becomes dark red in color if it be boiled with fuming nitric acid to which considerable water has been added (delicate reaction). Being an amido acid, tyrosine unites with acids and bases, forming salts. If it be heated to 270° it decomposes into carbon dioxide and oxyphenylethylamine, C₆II₄(OH). CH₂. CH₂. NH₂. When fused with caustic potash it yields paraoxybenzoic acid, ammonia and acetic acid. Putrefaction causes the formation of hydroparacoumaric acid, and nitrous acid converts the tyrosine into para-oxyphenyl-lactic acid (A. 219, 226).

4. β -Phenyl-hydracrylic Acid, C_6H_5 . CH(OH). CH₂. CO₂H, commonly called *phenyl lactic acid*, results on boiling β -bromhydrocinnamic acid with water (A. 195, 138), and in the reduction of benzoyl acetic ester, as well as by the addition of hypochlorous acid to cinnamic acid, and then reducing the resulting chlor-acid with sodium amalgam. The acid melts at 93°. When heated with dilute sulphuric acid it decomposes (like the aliphatic β -oxy-acids) at 190° into water and cinnamic acid (together with a little styrolene) (B. 13, 304). When digested with the haloid acids it forms phenyl- β -haloid-propionic acids.

o., m., and p. Nitrophenyl-lactic Acids, or hydracrylic Acids, NO₂. C₆H₄CH(OII). CH₂. CO₂H, melt at 126°, 105°, and 132°. The three isomerides result upon treating the three nitro-β-bromhydrocinnamic acids with sodium carbonate, when (in the cold) O—CO

the o-, m-, and p-nitrophenyl-lactic acid lactones, NO₂C₆H₂CH₃. The melting at 124°, 98°, and 92°, are also produced. These are the only β-lactones known (B. 17, 595).

595).

The ortho-nitro-acid results, further, by oxidizing the aldehyde first produced with silver oxide (B. 16, 2206). When heated to 190° with dilute sulphuric acid it yields o-nitrocinnamic acid. Its lactone decomposes on boiling with water into carbon dioxide and o-nitrostyrolene; it yields β-oxyhydrocarbostyril when reduced.

When the three nitro-acids are heated with alcoholic zinc chloride, we do not get their

Lesciones, but their esters (B. 17, 1659).

β-Chlor-, brom-, and iodhydrocinnamic acids, C₆H₅. CHX. CH₂. CO₂H, melt 126°, 137°, and 120°. They are obtained from cinnamic acid or $\bar{\beta}$ -phenylacrylic **acid** by the addition of halogen hydrides in aqueous or glacial acetic acid solution (B. **22**, 1221), and from β -phenylhydracrylic acid (see this). When heated or boiled with water the free acids decompose, with previous formation of \(\beta\)-oxyacids, into halogen by dride and cinnamic acid. When neutralized, even in the cold, with alkali carbonates

they break down into haloid acid, carbon dioxide, and styrolene, C₆H₅. CH: CH₂.
 o, m., and p.Nitro-β-bromhydrocinnamic Acids, NO₂C₆H₄CHBr. CH₂. CO₂H,
 Per produced by the addition of hydrogen bromide in glacial acetic acid to the three

Distrocinnamic acids (B. 17, 596, 1494) (see also nitrophenyl-lactic acid lactone).

β-Amidohydrocinnamic Acid, C₆H₈. CH(NH₂)CH₂. CO₂H, melts at 120° (B. **27, 1498**; A. 200, 97).

y- and d-Oxyacids.—y-Oxyacids, beginning with the phenyloxybutyric acids, are known. They pass readily into their lactones. γ-Phenyl-γ-oxybutyric Acid, CaH₅.-CH(OH). CH₂. CH₃. CO₃H, melts at 75°, and slowly decomposes even from 65-70° anto water and its lactone—phenyl-butyrolactone, C₁₀II₁₀O₃. The latter melts at 37° **≈nd** boils at 306°.

It is obtained from β -benzoyl propionic acid (p. 261) (B. 15, 889) and from phenylbrombutyric acid. Its lactone is formed on boiling phenylisocrotonic acid and phenyl-

persconic acid with dilute sulphuric acid (A. 228, 178; B. 29, R. 14).

a-Phenyl-y-oxyvaleric Acid, only stable in the form of liquid lactone (B. 17, 73). b-Benzyl-y-oxyvaleric Acid melts at 101° and its *lactone* at 33° (A. 268, 94).

β-Benzyl-y-oxyvaleric Acid melts at 75° and its lactone at 86° (A. 254, 215). is obtained from benzal-lævulinic acid.

a-Benzyl-o-oxyvaleric Acid (B. 24, 2447).

B. Dioxyalcohol Acids are chiefly obtained by oxidizing the phenyl-olefine-carboxylic acids with potassium permanganate (A. 268, 44; 283, 338). The two possible phenyl

glyceric acids are known.

Atroglyceric Acid, a-Phenylglyceric Acid, CH2OH. C(C6H5)OH. CO2H, melting at 146°, results on boiling a, β -dibromhydroatropic acid with excess of alkalies, and from benzoyl carbinol by means of prussic acid and hydrochloric acid (B. 16, 1292). It breaks down into CO, and phenylacetaldehyde upon heating.

Dibromhydratropic Acid, CH₂Br. C(C₆H₅)Br. CO₂H, melting at 115°, is produced when bromine acts upon atropic acid. It decomposes on boiling with water into aceto-

phenone, CO₂, and HBr.

Styceric Acid, β-Phenylglyceric Acid, C₆H₅. CHOH. CHOH. CO₂H, melting at 141° with decomposition (A. 268, 37), is obtained by first getting the dibenzoyl ester and saponifying it, or by boiling phenyl-a-chlorlactic acid with water; also by oxidizing cinnamic acid with potassium permanganate. Heated above its melting point, it decomposes into phenylacetaldehyde, carbon dioxide, and water. Hydrobromic acid converts it into phenyl-3-brom-lactic acid (B. 16, 1289). The dibenzoyl-acid melts at 187°.

The dibensoyl methyl ester melts at 113°.

The dibensoyl ethyl ester melts at 100° (B. 12, 538). p. Nitrophenylglyceric Acid, melting at 167°, is obtained from p-nitrophenylglycidic

o-Amidophenylglyceric Acid melts at 218°.

Phenyl-a-chlorlactic Acid, C₆H₅. CH(OH)CH. Cl. CO₂H + H₂O, melts at 56°, and when anhydrous at 86°. It results from the action of hypochlorous acid upon cinnamic acid. Sodium amalgam reduces it to phenyl-lactic acid, alkalies change it to phenylglycidic acid and phenylglyceric acid, while with fuming hydrochloric acid it

pleds phenyldichlorpropionic acid (B. 22, 3140).

Phenyl-a-bromlactic Acid, C₆H₅. CH(OH). CHBr. CO₂H + H₂O, melts at 125° when anhydrous. It is formed on boiling phenyldibrompropionic acid with water (B. 13, 310). It has been separated by means of cinchonine into two optically active

components (B. 24, 2831).

Phenyl-a-iodlactic Acid, CaHs. CH(OH). CHI. CO2H, melts at 137° with decomposition. It results from the action of an aqueous chloriodine solution upon cinnamic acri. 3. 13. 2414. • o- and p-Mitrophenyl-o-chloriactic Acids mek at 119° and 165°. The o-rody is converted by sodium amalgam into indol. (B. 13, 2261; 19, 2646).

- Narochenyl-e bromlactic Acid melis at 1450 (B. 17, 219).

Pheny! - amidolactic Acid. Pierriaria, C.H., CH(OH)CH(NH,)CO,H+H,O, tecomposes, when analytic es. at 1193. It results from the action of acids upon the Phenyl-3-chloriactic Acid. C_{H3}. CHCl. CHOH CO_H, melting at 141°, and Phenyl-3-chloriactic Acid are produced when fusing haloid acids act upon phenyl-3-chloriactic Acid are produced when fusing haloid acids act upon phenyl-3-chloriactic Acids, melting at 125° and 167°, are obtained by the action of fusing hydrochloric acid upon the oxresponding giverdic acids. B. 19, 2040).

c-Nitrophenyl-3-bromlactic Acid melts at 135° (B. 17, 221).

Cinnamic Acid Dichloride, c.3. Dickissendracionamic Acid, CaHa. CHCI. CH. C. CO, H. melting at 103°, results when chlorine acts upon cinnamic acid in carbon issuitable solution and on treating phenyl-a-chloriactic acid with fuming hydrochloric and B. 14, 1867).

Allocinnamic Acid Dichloride is an oil decomposable by strychnine into two

optically active components (B. 27, 2041).

Cinnamic Acid Dibromide, a,3-Dicromkriro-innamic Acid, melting at 1950, yiel is (10), phenylacetal dehyde, cumamic acid, and phenyl-a-bromlactic acid on boiling with water. Strychnine resolves it into two optically active components (B. 26, 1664). The restriction melts at 1170. The ethyl ester melts at 600 (B. 22, 1181).

Allocinnamic Acid Dibromide melts at 91-93°. It is separated into two optically tree components by cinchonine (B. 27, 2039). The methyl ester melts at 52-53°.

active components by cinchonine (B. 27, 2039). The methyl ester melts at 52-53° o and p Nitro-a, 3-dibromhydrocinnamic Acids melt at 180° and 227°. o- and p-circl exters melt at 71° and 110° (A. 212, 151).

Phenylglycidic Acid, CaHs. CH-CH. CO.H., separated from the sodium salt, is an oil solidifying at c?. It results from the action of alkalies upon a- and 3-chlorphenyllivitic acids, as well as by the condensation of benzaldehyde with chloracetic ester (A. 271, 137. Phenylglycidic acid is very unstable. It readily decomposes into CO, and phenylaceta dehyde. On boiling with water phenylglyceric acid is also produced. optical y active phenylglycidic acids are obtained in the form of sodium salts from the optically active phenyl-a bromlactic acids.

o Nitrophenyl-glycidic Acid, NO₂[2]C₈H₄CH $\stackrel{\bigcirc}{\sim}$ CH . CO₂H $\stackrel{}{+}$ H₂O, melts at 64°, and at 125° when anhydrous. It is produced when alcoholic potash acts upon o introphenyl-lactic acid, or by the action of sodium hypochlorite upon o-nitrophenyllactic acid ketone (A. 284, 135). It breaks down, on heating, into CO₂ and indigo. It yields anthranil and anthroxanaldehyde on boiling with water (p. 249) (B. 19, 2649).

p Nitrophenyl-glycidic Acid melts with decomposition at 186° (B. 19, 2644).
C. Trioxyalcohol Acids.—y-Phenyltrioxybutyric Acid, C₆H₃[CH.OH]₃CO₂H, passes readily into the lactone, melting at 115–117°; by reduction this yields phenyltettore (p. 248). y-Phenyltrioxybutyric acid is prepared by reduction this yields phenyltettore (p. 248). to e (p. 248). y Phenyltrioxybutyric acid is prepared by starting with the dibromide of cum unic aldehyde cyanhydrin (B. 25, 2556).

7. PHENYLPARAFFIN-ALDEHYDE CARBOXYLIC ACIDS.

A explained under the aliphatic unsaturated ketols, oxyolefine carboxylic acids and explicione carboxylic acids (1, 318), the oxymethylene derivatives are produced by the condensation of acetone, acetic ester, acetoacetic ester, and other bodies with formic redet in the presence of sodium ethylate. As these compounds conduct themselves in many respects like aldehydes, it was originally supposed that they contained the aldehyde group, and it was only their very pronounced acid character which led to considering them as a specific proposed in the compounds. It is rather remarkable that two isomeric esters are formed in the condensation of phenylacetic ester and formic ester by means of sodium cthylate. Buth budies yield the same derivatives with phenylhydrazine. The one is a liquid and the other a solid. The latter is distinguished from the former by its stronger acid character. It changes to the liquid modification on being heated. Carbonic acid precipitates from alkaline solutions of the esters the liquid, more feebly acid modification, whereas when an excess of mineral acid is added it is the solid, more acid modification which separates (see nitrophenyl methane, p. 178). W. Wislicenus believes that it is the solid modification which corresponds to the real phenyl formylacetic ester (B. 29, 742). Oxymethylenephenylacetic Ethyl Ester, CH(OH): C(C₆H₅)CO₂C₃H₆, is a liquid

boiling at 144° (16 mm.). Ferric chloride imparts a violet color to it.

Phenylformylacetic Éthyl Ester, CHO. CH(C6H5)CO2C2H5, melts at 70°, passing at the same time into the liquid isomeric ester.

8. PHENYLPARAFFIN-KETONE CARBOXYLIC ACIDS.

The acids belonging in this group can be arranged, like the aliphatic **ketone-carboxylic** acids, into a-, β -, and γ -ketone-carboxylic acids, and in each of these groups we can have sub-groups, depending upon whether the ketone group is in direct union with the benzene nucleus or not.

A. a-Ketone-carboxylic Acids result from (1) the oxidation of ketones; (2) of glycols; (3) of ketone alcohols; (4) of alcohol carboxylic acids; (5) (nucleus-synthetic) from cyanides of the acid radicals by saponification with cold, concentrated hydrochloric acid; (6) from benzenes by the action of chloroxalic esters in the presence of aluminium chloride (B. 20, 2045).

Phenylglyoxylic Acid, Benzoyl Formic Acid, C.H. CO.CO.H, melting at 65° and isomeric with the phthalaldehydic acids, is obtained by oxidizing acetophenone with potassium ferricyanide (B. 20, 389), as well as by oxidizing phenyl glycol, benzoyl carbinol, and mandelic acid with dilute nitric acid:

$$C_6H_6$$
. CO . CH₃ \longrightarrow
 C_6H_6 . CH (OH) . CH₂OH \longrightarrow
 C_6H_6 . CO . CO₂H.
 C_6H_6 . CO . CO₂H.

The acid was first prepared (in a nucleus-synthesis way) by saponifying benzoyl cyanide, its nitrile, obtained from benzoyl chloride and mercury, or silver cyanide (Claisen). Its ethyl ester is formed when ethyl chloroxalic ester acts upon mercury diphenyl, or upon benzene in the presence of AlCl₃.

The acid is very soluble in water, and when distilled decomposes into CO, and benzaldehyde. When mixed with benzene containing thiophene and sulphuric acid, it is colored deep red, afterward blue-violet; all its derivatives, and also isatin, react simi-

Being a ketonic acid it unites with sodium bisulphite and with CNH (see phenyl tar-Sodium amalgam converts it into mandelic acid, and hydriodic acid into tronic acid).

a toluic acid.

Its methyl ester boils at 247°. Its ethyl ester boils at 257°. The a-amide melts at 90°. The β-amide hydrate, C₆H₆. CO. CONH₂ + H₂O, melts at 64°. The γ-amide melts at 134° (B. 12, 633; 20, 397). The anilide, from γ-benzil monoxime (see this) and PCl, melts at 63°.

Benzoyl Cyanide, CaH5. CO. CN, melting at 32° and boiling at 207°, is obtained in the distillation of benzoyl chloride with mercuric cyanide, and by the action of acetyl chloride (B. 20, 2196) upon isonitrosoacetophenone. Sodium in absolute alcohol converts it into polybenzoyl cyanide, (C₂H₂NO₂)x, melting at 95° (J. pr. Ch. [2], 39, 260). Alkalies change benzoyl cyanide to benzoic acid and potassium cyanide, while concentrated hydrochloric acid converts it into benzoyl-formic acid. Chlorisonitrosoacetophenone, bensoylformoximic acid chloride, CaH6. CO. C(: NOH)Cl, melting at 131°, is produced in the chlorination of isonitrososcetophenone (p. 249) (B. 26, R. 313).

Phenylhydrazimethylene Carboxylic Acid, $C_{ij}H_{ij}$. $C(<_{ij}NH_{ij})$. CO.H. The bydrazine salt melts at 119°. Diphenylglyoxylic Acid Hydrazone, $C_{\mathbf{c}}H_{\mathbf{s}}$. $\mathbf{C}(:\mathbf{N})CO_{\mathbf{s}}H$

Its diethyl ester melts at 138° (J. pr. Ch. [2], 44, 567).

C₆H₅. C(: N)CO₂H·

C₆H₅. C(: N)CO₂H·

Phenylglyoxylic Acid Phenylhydrazone melts at 138° (J. pr. Ch. [2], 44, 567).

Phenylglyoxylic Acid Phenylhydrazone melts at 147°. (a-), Anti-phenylglyoxylic Acid Oxime melts at 147°. (a-), Anti-phenylglyoxylic Acid Oxime, Isonitrosophenylacetic Acid, C₆H₅. C(: NOH)CO₂H, melts at 128° (B. 24, 42). The methyl ester melts at 138°. The dimethyl ester melts at 56° (B. 16, 519). Benzoyl Cyanide Oxime, C₆H₅. C(: NOH)CN, melting at 129° (B. 24, 3504), is obtained from benzyl cyanide by means of amyl nitrite and sodium or nitrous acid and sodium ethylate (A. 250, 162; B. 28, 1707). nitrous acid and sodium ethylate (A. 250, 163; B. 28, 1797).

Substituted Benzoyl Formic Acids. - o- and p-Brombenzoyl Formic Acids melt at

93°-103° and 108° (B. 25, 3298, and 28, 259).

o-Nitrobenzoyl Formic Acid, NO₂. C₂H₄CO. CO₂H + H₂O, melts at 47°, and when anhydrous at 122°. The amide melts at 199°. The nitrile melts at 54° (B. 23, 1577). The oxime when acted upon with water yields CO₂ and o-nitrobenzonitrile. Salicylic acid is produced when it is boiled with alkalies (B. 26, 1252). It forms two isomeric phenylhydracones (B. 23, 2080).

m-Nitrobenzoyl Formic Acid melts at 77°. The amide melts at 151°. The nitrile

melts at 230° (145 mm.) (B. 14, 1186).

o-Amidobenzoyl-formic Acid, Isatinic acid, is produced on reducing o-nitrobenzoyl formic acid with ferrous sulphate and sodium hydrate, and in the action of alkalies on isatin. If it be separated from its lead salt by means of hydrogen sulphide, and evaporated under greatly reduced pressure at low temperature, it is obtained as a white powder. Digestion of its solution converts it at once into its lactam or lactime—

Isatin, lactam of isatinic acid, CoH. \[\big(\big[\frac{1}{2} \big] \bigNH_\], or lactime of isatinic acid, C₆H₄{CO N C. OH (?), melting at 201°. It was first obtained by oxidizing indigo. It consists of orange-red prisms. It dissolves in the caustic alkalies with the formation of salts. The solution, violet at first, soon becomes yellow, owing to the production of isatinates. Isatin acts at the same time like a ketone.

Its other methods of formation and its derivatives will be discussed later in connection with the hydroindol derivatives. The isatin derivatives referable to the lactam formula are designated pseudo- or ψ -derivatives, or n-derivatives,—i. e., those in which the recently entered group is attached to nitrogen, - whereas the true isatin derivatives are referred to

the lactime formula, because the latter appears to belong to free isatin.

Aceto-isatinic Acid, CH₈. CO. NH[2]C₆H₄. CO. CO₂H, melting at 160°, results upon treating acetyl-ψ-isatin (see this) with alkalies, and then with acids. Benzoylisatinic Acid, melting at 188°, is produced when benzoyltetrahydroquinoline is oxidized

with KMnO₄ (B. 24, 772).

Acetyl-isatin, C₆H₄ { [1]CO.CO | Modern conditions of the condition of the c

at 206°.

Anthroxanic Acid, C₈H₄ { [1] C O CO₂H (?), melting at 190°, results upon oxidiz-

ing anthroxan aldehyde (p. 250) with potassium permanganate (B. 16, 2222).
p.Dimethylamidophenylglyoxylic Ester, (CH₃), N. C₆H₄CO. CO₅C₅H₅, melting at 187°, is obtained from dimethyl aniline and ethyl oxalic acid chloride (B. 10, 2081).
o-Oxyphenylglyoxylic Acid, from isatinic acid (B. 26, 221), melts at 43°.
p-Methoxyphenylglyoxylic Acid melts at 89°.

Veratroyl-carboxylic Acid, (CH₂O),[3,4]C₈H₃.CO.CO₂H, melting at 138°, and Piperonoyl-carboxylic Acid, (CH₂O₂)[3,4]C₈H₂CO.CO₂H, melting at 148°, have been produced by the oxidation of anethol, of isoeugenol methyl ether, and of isosafrol

(B. **24**, 3488).

Homologous Phenylglyoxylic Acids. - m - Tolylglyoxylic Acid yields so-called Methyl Isatin, CH₂[5]C₆H₃ { [1]CO.CO melting at 184°. This is obtained by boiling a methylicide a calculation of the control of the con ing p-methylisatin-p-tolylimide, melting at 259°, the product of the action of dichloracetic acid upon p-toluidine, with hydrochloric acid (B. 16, 2262; 18, 198).

```
M. P. . . 96° (B. 14, 1750; 20, 2049).
           Mesityl-glyoxylic Acid, . . 112-116° (B. 24, R. 741).
[2,4,5]-Pseudocumylglyoxylic Acid, . . . 75° (B. 24, R. 741).
2,3,4,6 and 2,3,5,6-Tetramethylphenylglyoxylic Acid, (B. 19, 233; 20, 3
                                                                         (B. 19, 233; 20, 3099).
```

Phenylpyroracemic Acid, C₆H₅. CH₂. CO. CO₂H, melts at 154° with evolution of carbon dioxide. It is formed when a benzoylamidocinnamic acid (A. 275, 8) is boiled with caustic alkali or hydrochloric acid, as well as by boiling phenyloxalacetic ester with dilute sulphuric acid (A. 271, 163).

o-Oxyphenylpyroracemic Acid, HO. Calla. CH2. CO. CO2H, is produced, like phenylpyroracemic acid, from a-benzoylamido-o-oxycinnamic acid and sodium hydroxide.

Its lactone, a-Oxohydrocumaein, C₆H₄ { [1]CH₂. CO (?), melting at 152°, is produced when it is boiled with acids (B. 18, 1187).

B. Phenylparaffin-β-Ketone Carboxylic Acids are produced (1) by a condensation, similar to the acetoacetic ester formation, from benzoic and fatty acid esters, acetophenone and carbonic acid esters, with alcohol elimination, in the presence of sodium alcoholate (see benzoyl acetic ester); (2) by the introduction of alphyl residues, by means of chlorides,—e.g., benzyl chloride,—into acetoacetic ester (see benzylacetoacetic ester); (3) by action of benzaldehydes upon diazoacetic ester (see benzoyl acetic ester).

With hydroxylamine they yield oxime anhydrides, lactoximes or isoxazolons; and with hydrazine and phenylhydrazine, hydrazine anhy-

drides, lactazams or pyrazolons (1, 362).

Benzoyl Acetic Acid, C.H. CO.CH, CO.H, melts at 103° with decomposition into CO, and acetophenone. It breaks down in the same manner when it is boiled with dilute acids. It is obtained by saponifying its ethyl ester with caustic potash at the ordinary temperature. Ferric chloride imparts a violet-red coloration to its solution.

Benzoyl Acetic Ester, C₆H₆. CO. CH₇. CO₂C₂H₆, boils at 148° (11 mm.). (1) It was first prepared by dissolving phenyl-propiolic ester in sulphuric acid and then diluting with water (B. 17, 66). (2) By

the action of sulphuric acid and water upon a-bromcinnamic ester (B. 19, 1392). (3) It is most conveniently made by the action of dry sodium ethylate or sodium upon ethyl benzoate and acetic ester (B. 20, 653, 2179). (4) Small quantities of the ester are produced when esters of carbonic acid act upon acetophenone together with sodium ethylate. (5) It is also formed when benzaldehyde is heated with diazo-acetic ester:

1.
$$C_6H_4$$
. $C \equiv C$. CO_3 . C_2H_6 SO_6H_8

2. C_6H_5 . $CH = CBr$. CO_3 . C_2H_5 H_5O

3. C_6H_5 . $CO_2C_3H_5 + CH_3$. CO_3 . C_2H_5 $-C_2H_5OH$

4. C_6H_5 . CO . CH_3 + C_3H_5O . CO_2 . C_2H_6 $-N_2$

5. C_6H_5 . $COH + N_2$. CH . $CO_3C_3H_6$ $-N_2$

Benzoyl Acetic Ester.

Benzoyl-acetic ester volatilizes with steam without decomposition (A. 282, 155). Its odor resembles that of acetoacetic ester.

It forms (I) with ammonia an addition product like that of aldehyde-ammonia; with amines it splits off water and yields imides—e.g., \(\beta\)-methylimidehydrocinnamic ester, \(^{1}_{6}\)-C(NCH_{3})CH_{2}\). CO₂. C₂H₅ (B. 29, 105); with (2) hydrazine it yields 3-phenylpyrazolon; (3) with phenylhydrazine, diphenylpyrazolon; (4) with hydroxylamine, phenylisoxazolon; (5) with urea, phenyluracil; (6) with guanidine, imidophenyluracil; (7) with nitrous acid, the oxime; (8) with diazobenzene chloride, the phenylhydrazone of benzoyl glyoxylic ester (p. 261); (9) with PCl₅, \(\beta\)-chlorcinnamic chloride. Iodine converts its sodium compound into dibenzyl-succinic ester, while with the alkylogens homologous benzoyl acetic esters result. The hydrogen atoms of the CH2 group are also replaceable, step by step, by acid radicals. It yields β -ethoxycinnamic esters when acted upon with orthoformic esters. The amide melts at 112° (A. 266, 332), and the anilide at 107° (A. 245, 374).

Benzoyl Acetonitrile, ω Cyanacetophenone, C₄H₅. CO. CH₄. CN, melting at 80°, is produced on boiling benzoylcyanacetic ester (p. 263) with water, on acting upon sodium oxymethylene acetophenone with hydroxylamine hydrochloride and sodium hydroxide (B. 24, 133), and upon treating imidobenzoylacetonitrile or imidobenzoyl methyl cyanide

with hydrochloric acid.

Imidobenzoyl Cyan-methane, Calla. C(: NH)CII2CN, melting at 86°, results when sodium acts upon a dry ethereal solution of benzonitrile and methyl cyanide or acetonitrile (B. 22, R. 327). When treated with hydroxylamine hydrochloride, the imidegroup is replaced by the oximido group, and the latter adds itself to cyanogen with the

production of phenylisoxazolonimide, $C_6H_5C.CH_2.C:NH$, melting at 111° (B. 26, R. 272).

p-Nitrobenzoyl-acetic Acid, C₆H₄(NO₂). CO. CH₂. CO₂H, melts at 135°, and is produced by heating p-nitrophenyl propiolic ester with sulphuric acid. It breaks down, on melting, into CO, and p nitroacetophenone. o Nitrophenyl propiolic ester is readily

transposed into the isomeric isatogenic ester (B. 17, 326).

Methylbenzoyl-acetic Ester, boiling at 226° (225 mm.), when treated with nitrous acid forms a isonitrosopropiophenone (B. 21, 2119). Ethyl- and diethylbenzoylacetic ester boil at 210° (90 mm.) and 223° (150 mm.).

Allyl-benzoyl-acetic Ester boils at 220° (100 mm.). Benzoyltrimethylene Carboxylic Acid, melting at 148°, decomposes at higher temperatures into CO, and bentoyl-trimethylene (pp. 23, 190) (B. 16, 2128, 2136).

2,5-Dinitrophenyl- and 2,4,6-Trinitrophenyl acetoacetic Eater, melting at 94°

and 98°, result from the action of 2,5-dinitrobrombenzene and 2,4,6-trinitrochlorbenzene

(p. 68) upon sodium acetoacetic ester (A. 220, 131; B. 22, 990; 23, 2720).

Benzylacetoacetic Ester, C₆H₅. CII₂. CH<

CO₂CH₃, is derived from sodium

acetoacetic ester and benzyl chloride (A. 204, 179). It boils at 276° and by the ketone decomposition yields benzyl acetone (B. 15, 1875) (p. 190); by the acid decomposition nt forms phenylpropionic acid (p. 197).

D. γ- and δ·Ketone Carboxylic Acids.
β-Benzoylpropionic Acid, C₄H₅. CO. CH₂. CH₃. CO₂H, melting at 116°, is obtained (1) by the condensation of benzene and succinic anhydride by means of AlCl₃ (B. 20, 1376); (2) by reducing β -benzoyl acrylic acid; (3) by the elimination of carbon dioxide from benzoylisosuccinic acid (p. 262), and (4) from phenacyl-benzoylacetic ester by the acid decomposition; (5) by boiling the HCN-addition-product of cinnamic aldehyde with dilute hydrochloric acid, and carefully saponifying the phenyloxycrotonic acid produced at first in the cold, which in the heat rearranges itself (B. 29, 2582):

-
$$C_0H_5CH = CH$$
 . $CH(OH)CN \xrightarrow{\longrightarrow} C_0H_5CH = CH$. $CH(OH)$. $COOH \xrightarrow{\longrightarrow} C_0H_5$ - $COOH$. $COOH$.

It dissolves with difficulty in hot water. Sodium amalgam reduces it to γ -phenylbutyrolactone.

Phosphorus pentasulphide converts the acid into phenyloxythiophene (B. 19, 553). It yields two isomeric oximes, melting at 129° and 92° (B. 25, 1932).

•-Phenyl-lævulinic Acid, C₆H₅. CH < CO₂H₁ CO₁CH₃, melting at 126°, is derived from phenylacetosuccinic ester (B. 17, 72; 18, 790). β Benzyl-lævulinic Acid, C_8H_5 . CH_2 . CH_3 . CO_2H , from β -benzal-lævulinic acid (A. 254, 202), melts at 98°. See benzalangelicalactone. β -Phenyl- γ -acetobutyric Acid,

C₆H₅. CH

CH₂. CO. CH₃, melts at 83°. It is obtained from phenyldihydroresorcinol

by the action of alkalies or acids (B. 26, 2057; A. 294, 322). Phenyldihydroresorcinol

is again formed when its esters are condensed with sodium alcoholate.

9. PHENYL-ALCOHOL-KETONE CARBOXYLIC ACIDS.

Benzoyl Glycollic Acid, C₆H₅. CO. CH(OH)CO₂H, melts at 125° (B. 16, 2133). Phenyl-γ-keto-α-oxybutyric Acid, C₆H₅. CO. CH₂. CH(OH)CO₂H, melting at 125°, is obtained from its trichloride, chloral acetophenone, C₆H₅. CO. CH₂. CH-(OH)CCl₂, melting at 76° (B. 26, 557).

10. DIKETONE CARBOXYLIC ACIDS.

Benzoyl Glyoxylic Acid, C₆II₆. CO. CO. CO₂II. The a-oxime and a-phenylhydrazone of the ethyl ester of this acid have been prepared by the action of nitrous acid

and diazobenzene chloride (B. 21, 2120) upon benzoyl-acetic ester (p. 259).

Benzoyl-isonitroso-acetic Ester, C₆H₆. CO. C(: NOH)CO₂C₂H₆, melts at 121°.

Benzoyl-a-phenylhydrazone-glyoxylic Ester, C₆H₆. CO. C(: N. NHC₆H₆)CO₂-

C, H, melts at 65

Quinisatinic Acid, o-Amidobenzoyl Glyoxylic Acid, NH₂[2]C₆H₄CO.CO.-CO, II, at 120° breaks down into water and its lactam or lactime. It is obtained by oxidizing β , γ -dioxycarbostyril with ferric chloride. Its lactam or lactime is—

Quinisatin, C_6H_4 [1]CO . CO
Quinisatin, C_6H_4 [2]NH . CO C_6H_4 [2]N = COH, melting at 255-260° (B.

17, 985). Benzoyl Pyroracemic Acid, C₆H₅.CO.CH₂.CO.CO₂II, melting at 157°, is prepared from its *ethyl ester* (melting at 43°), produced in the condensation of acetophenone and oxalic ester (B. 21, 1131). Ferric chloride imparts a blood-red color to the alcoholic solution of the ester.

When benzoyl chloride acts upon acetoacetic ester it produces benzoyl acetoacetic ester, C2H5. CO. CH. (CO. CH2). CO2C2H5. This decomposes into acetophenone and

benzoyl acetone (B. 18, 2131).

o-Nitrobenzoyl-aceto-acetic Ester (A. 221, 323).

Acetophenone-acetoacetic Ester, C₈H₅.CO.CH₂.CH.CO.CH₃ melts at 130°-140°, with decomposition into CO, and acetophenone-acetone (p. 249). Its ethyl ester is produced by the action of ω -bromacetophenone upon sodium acetoacetic ester (B. 16, 2866). Like acetophenone-acetone, the ester readily forms a furfurane derivative.

II. PHENYLPARAFFIN DICARBOXYLIC ACIDS.

The phenylparaffin dicarboxylic acids, like the aliphatic, saturated dicarboxylic acids.

can be arranged into malonic acids, ethylene succinic acids, etc.

Phenylmalonic Acids.—Phenyl Malonic Acid, CaH₅. CH(CO₂H)₂, melts at 152°, splitting off CO, and forming phenyl acetic acid. Its ester, boiling at 1710 (14 mm.), is formed from phenyloxalacetic ester by the elimination of carbon monoxide (B. 27, 1091). Dinitrophenylmalonic Ester, (NO₂)₂. C₆H₃. CH(CO₂C₃H₅)₃, melting at 51°, is obtained by the action of bromdinitrobenzene upon sodium malonic ester (B. 21, 2472; 22, 1232; 23, R. 460; 26, R. 10).

2,4,6 Trinitrophenylmalonic Ester, *Picrylmalonic Ester*, (NO₃)₃C₄H₅CH(CO₄-C₄H₅)₂, exists in two modifications, melting at 58° and 64° (B. 28, 3066; 29, R. 997).

Benzyl Malonic Acid, β. Phenylisosuccinic Acid, CaH, CH, CH(CO, H), melting at 117°, is obtained from its ester, produced in the action of benzyl chloride upon sodium malonic ester, as well as by the reduction of benzal malonic acid (p. 288) (A. 218, 139).

o- and p-Nitrobenzyl-malonic Ester (B. 20, 434).—The o-acid is condensed by sodium hydroxide to n-oxy-a-indol-carboxylic acid (B. 29, 639). Methylbenzyl

Malonic Acid (A. 204, 177).

Phenylsuccinic Acids.—Phenyl-succinic Acid, CaH, CH, CO, H CH₂. CO₂H' melting at 167°, results from ω-chlorstyrene, C₆H₅. CH: CHCl, as well as from benzal malonic ester, by means of potassium cyanide (A. 293, 338); by the decomposition of phenylacetsuccinic ester, by means of very concentrated caustic potash; from phenyl-ethanetri carboxylic acid (p. 264), and from the so called hydro-cornicularic acid, C11 H16O6. lts anhydride melts at 54° (B. 23, R. 573).

Oxyphenylsuccinic Acid melts with decomposition at 150°. It is obtained from

coumarin and potassium cyanide (A. 293, 366). CH₃, CHCO₂H, have been obtained in two Phenyl-methyl-succinic Acids, modifications, melting at 170° and 192° (B. 24, 1876).

C₆II₅. CII₂. CH. CO₂H CH₂. CO₂H, melts at 161°, and results from Benyzlsuccinic Acid.

sodium ethan-tricarboxylic ester, or sodium ethan-tetracarboxylic ester by the action of benzyl chloride, etc. (B. 17, 449), as well as by the reduction of phenyl-itaconic acid (B. 23, R. 237). It forms an anhydride, melting at 102°.

12. PHENYL-ALCOHOL-DICARBOXYLIC ACIDS.

Benzyl Tartronic Acid, C₆H₅. CH₂. C(OH)(CO₂H)₂, melts at 143°, with decomposition into CO₂ and 3-phenyl-lactic acid (p. 252). It results from the action of caustic potash on benzylchlormalonic ester, the product obtained from the interaction of benzyl chloride and sodium chlormalonic ester (A. 209, 243). a-Anilido-, Phenyl-hydrasidobenzylmalonic Ester, etc., are produced by the addition of the respective bases to benzal-

malonic ester (B. 28, 1451; 29, 813).

\$\beta\$ Methoxybenzyl Malonic Acid, \$C_6H_5\$. CH(OCH_3). CH(CO_5H)_2\$, melts at 115° with decomposition into methyl alcohol and benzal malonic acid, from whose ester the β-methoxybenzylmalonic ester is produced by addition of sodium methylate (B. 27, 289).

C₆H₅. C(OH)CO₂H CH, . CO,H, melting Phenylmalic Acids.—a-Phenyl-a-oxysuccinic Acid, at 187°, is produced by the action of bromine, phosphorus and water upon phenylsuccinic acid.

a-Phenyl- β -oxysuccinic Acid, C_6H_5 . CH. CO_2H , CH(OH). CO, H, melting at 150-160°, results from the interaction of phenylformylacetic ester, prussic acid, and hydrochloric acid (B. 23, R. 573).

Phenyl-itamalic Acid may be obtained in the form of its lactone acid, Phenylparaconic Acid, C₈H₅.CH.CH—CO₂H
O—CO CH₂, melting at 109°, by heating benzaldehyde

with sodium succinate and acetic anhydride (1, 492) (A. 256, 63). When phenyl-paraconic acid is boiled with alkalies it yields the salts of phenyl-itamalic acid. The latter, when in a free condition, immediately reverts to phenyl-paraconic acid. This, upon distillation, breaks down into carbon dioxide, phenylbutyrolactone (p. 254) and phenylisocrotonic acid. A further product is a-naphthol (see this).

Phenyl-itaconic acid is produced when metallic sodium or sodium ethylate acts upon phenylparaconic esters (p. 289). Hydriodic acid reduces it to benzyl succinic acid and

phenyl-butyric acid (B. 29, 15).

o-, m-, p-Chlorphenyl-paraconic Acids result from the condensation of monochlorbenzaldehydes with sodium succinate, and yield three chlorinated naphthols (B. 21, R. 733). 1,3,4-Dichlorphenylparaconic Acid, melting at 138°, forms two dichlornaphthols (B. 29, R. 224).

a- and β-Methylphenyl-paraconic Acids are produced in the condensation of a mathyl-g-parhthols (A. 255, 257).

benzaldehyde with pyrotartaric acid, and yield methyl-a-naphthols (A. 255, 257).

a-Phenyl-γ-valerolactone Carboxylic Acid, C₆H₅. CH. CO O, melting at 167°, CO₂H. CH. CH—CH₈ is produced in the reduction of phenylaceto-succinic ester (B. 18, 791).

13. PHENYLKETONE DICARBOXYLIC ACIDS.

Benzoyl Malonic Ester, C_6H_5 . CO. $CH(CO_2 \cdot C_2H_5)_2$, and o-Nitrobenzoylmalonic Ester, are produced by the action of benzoyl chloride and o-nitrobenzoyl chloride upon sodium malonic ester (B. 20, R. 381). The latter yields quinoline derivatives upon reduction (B. 22, 386).

Benzoyl Cyanacetic Methyl Ester, C_6H_5 . CO . $CH.< \frac{CO_3}{CN}$. CH_3 , melting at 74°, is formed from cyanacetic methyl ester (1, 440) and benzoyl chloride. Its ethyl ester, melting at 41°, from benzoyl acetic ester and cyanogen chloride, yields cyanacetophenone on boiling with water (p. 258).

Benzoyl-Isosuccinic Ester, C₆H₅. CO. CH₂. CH(CO₂C₂H₅)₂, is obtained from

ω-bromacetophenone and sodium malonic ester (B. 18, 3324).

C₆H₅. CH. CO. CO₂. C₂H₅, is formed from oxalic ester, Phenyl-oxalacetic Ester, CO₂. C₂H₅, phenylacetic ester, and sodium (B. 20, 592). See phenyl-malonic acid, p. 262.

C₈H₅. CH. CO. CO₂C₂H₅, is obtained from oxalic

ester, benzyl cyanide, and sodium (A. 271, 172). See phenylpyroracemic acid, p. 259.

C₆H₅. CH. CO₂H

is formed from sodium acoto

Phenyl-acetosuccinic Ester, CH₂, CO . CH . CO₂H, is formed from sodium acetoacetic ester and phenylbromacetic ester (B. 17, 71).

CeH₅. CH₂. CH₃. CO₂H

CH₃. CO. CH. CO,H, results from the interac Benzyl-aceto-succinic Ester, tion of sodium acetosuccinic ester and benzyl chloride (B. 11, 1058).

14. PHENYL-OXYKETONE DICARBOXYLIC ACIDS.

Ketophenylparaconic Ester, C₆H₅. CH. CH—CO₂C₂H₆, (B. 26, 2144).

15. PHENYLPARAFFIN TRICARBOXYLIC ACIDS.

Phenylcarboxyl-succinic Acid, Phenyl-ethane-tricarboxylic Acid.—Its ester is formed when phenylchloracetic ester acts upon sodium malonic ester (A. 219, 31). The acid breaks down, on heating, into CO, and phenylsuccinic acid (B. 23, R. 573).

16. PHENYLKETO-TRICARBOXYLIC ACIDS.

a and β -Benzoyltricarballylic Acids, C_aH_b . CO. CH(COOH)CH(COOH)CH, COOHI and C_aH_b COC(COOH)(CH_cCOOH). Their esters are formed from chloraccinic ester and benzoylacetic ester, or from benzoylacetic ester with bromacetic ester and sodium ethylate (B. 29, R. 788).

Addendum.—A number of compounds attach themselves to the phenylpolyalcohols and their oxidation products. They may be regarded as derived from the various classes of bodies which have just been described, by assuming, in addition to the one aliphatic side-chain, a second or more groups (mostly carboxyl groups) attached to the benzene ring. Most of the bodies belonging here are o-di-derivatives of benzene, o-phenylene derivatives, obtained in part from o-phthalic acid, and in part by the oxidation of derivatives of ortho-condensed hydrocarbons -e, g, indene and naphthalene. Mention may be made of the subjoined compounds. Some of them are intimately related to the dicarboxylic acids, which have been discussed, carrying the one carboxyl group in the nucleus and the other in the side chain.

17. PHENYLENE-OXYDICARBOXYLIC ACIDS.

o-Carbomandelic Acid, CO2H[2]C6H4. CH(OH)CO2H, decomposes readily into water and a lactone carboxylic acid:

Phthalid-carboxylic Acid, C_6H_4 $\binom{CH \cdot CO_2H}{CO}$, melting at 149°, and beyond 180° decomposing into carbon dioxide and phthalide. It is produced by reducing phenylglyoxyl-o-carboxylic acid (B. 18, 38t). It is quite soluble in water and crystallizes in leaflets.

Phthalid-acetic Acid, C₆H₄ {CH · CH₂ · CO₂H , melting at 150°, is derived from

phthalylacetic acid by reduction (p. 289) (B. 10, 1558, 2200).

Normeconine-acetic Acid, (IIO)₂[5,6]C₆H₂{[1]CH—CH₂. CO₂H melting at 228°, results from the action of hydriodic acid upon meconine-acetic acid, (CII₃O)₂[5,6]C₆H₂{[1]CH.CH₂.CO₂H tolder the condensation of opianic acid with malonic acid, glacial acetic acid, and sodium acetate (B. 19, 2295).

Dihydroisocoumarin-carboxylic Acid, C₆H₄ { [1]CH₂. CH. CO₂H, melting at [2]CO = 0

sults from the reduction of phthalylpropionic acid (B. 11, 1681).

o-Phenylene-aceto-glycol-lactone Acid, $C_6H_4\{[1]CH(CO_2H)O + 1\frac{1}{2}CH_2CO + 1\frac{1}{2}CH_2CO\}$ melting at 85°, is obtained from phenylene diacetic acid, bromine, phosphorus, and water (B. 26, 223).

o-Carbophenylglyceric Acid Lactone, C₆H₄ { [1]CH(OH) . CH . CO₂H , melting 202°, is produced when 8 contains at 202°, is produced when β -naphthoquinone is oxidized with a bleaching lime solution. When the lactone acid is heated with hydrochloric acid it loses water and becomes o-carbon-a-oxycinnamic acid lactone (B. 27, 198).

18. PHENYLENE KETONE DICARBOXYLIC ACIDS.

o-Carbophenylglyoxylic Acid, Phthalonic Acid, C₆H₄ { [1]CO · CO₂H , melting at 138-140°, is formed in the oxidation of o-hydrindene carboxylic acid (see this), naphthalene, a-naphthol, β -naphthol, and the oxy-quinone of β -phenylnaphthalene with potassium permanganate (A. 240, 142). It yields o-carbo-mandelic acid upon reduction (p. 264).

Trichloraceto-benzoic Acid, C₆H₄ { [1] CO. CCl₂, melting at 144°, and Tribromaceto-benzoic Acid, melting at 160°, result when chlorine or bromine, in glacial acetic acid, acts upon phthalylacetic acid (B. 10, 1556).

o-Carbobenzoyl Acetic Acid, C₆H₄ { [1]CO. CH₂. CO₂H, melting at 90°, with

decomposition into carbon dioxide and acetophenone-o-carboxylic acid (p. 238), is formed when phthalyl acetic acid is dissolved in an excess of caustic soda and precipitated with acids (B. 10, 1553).

Cyanacetophenone-o-carboxylic Acid melts at 136° (B. 26, R. 371).

Benzoyl-cyanacetoester-o-carboxylic Acid, $CO_2H[2]C_8H_4$. CO. $CH < \frac{CO_2C_2H_5}{CN}$ melting at 1210, is produced by the action of soda upon phthalylcyanacetic ester (B. 26, R. 370).

o-Carbobenzoyl-propionic Acid, C_6H_4 $\left\{ \begin{bmatrix} 1 \end{bmatrix} CO \cdot CH_2 \cdot CH_3 \cdot CO_2H \right\}$, melts at 137°. The double lactone, C_6H_4 $\left\{ \begin{matrix} CO_4 \\ CO_4 \end{matrix} \right\}$ o, corresponding to this acid, is produced on heating succinic anhydride and phthalic anhydride with sodium acetate (B. 11, 1680; 18, 3119).

19. TRI- AND TETRA-CARBOXYLIC ACIDS.

Benzylmalon-o-carboxylic Acid, o-Carbobensylmalonic Acid,

{CH₂.CH(CO₂H)₂, breaks down at 190° into hydrocinnam-o-carboxylic acid and

CO₂. Its diethyl ester results from the reduction of phthalylmalonic ester (A. 242, 37). o-, m-, p-Xylylene-dimalonic Tetra-ethyl Esters, CaH4[CH2. CH(CO2C2H5)2]2, are produced in the reduction of the three corresponding xylylenedichlor-dimalonic esters, C₆H₄[CH₂CCl(CO₂C₂H₆)₂]₂, which are the products of the action of sodium chlormalonic ester upon the e-xylylene dibromides (B. 21, 31). The xylylene dimalonic acids break down, on heating, into phenylene dipropionic acids and 2CO₂.

20. OXYTRI- AND PENTACARBOXYLIC ACIDS.

Phthalyl Diacetic Acid, C_6H_4 $\begin{cases} C[CH_3, CO_2H]_2 \\ COO \end{cases}$, melting at 158°, is obtained from phthalyl dimalonic acid, C_6H_4 $\begin{cases} C(CH)(CO_2H)_2)_3 \\ COO \end{cases}$ (A. 242, 80).

21. KETONE TRICARBOXYLIC ACIDS.

2,6-Dicarbophenylglyoxylic Acid, (CO₂H)₃[2,6]C₆H₃CO. CO₂H, melting at 238°, is formed when naphthalic acid is oxidized with KMnO₄ (B. 26, 1798). Hydriodic acid and phosphorus reduce it to 2-methylisophthalic acid (p. 242), and when heated it becomes 2-aldehydoisophthalic acid (p. 245), while more complete oxidation converts it into hemimellitic acid (B. 29, R. 282).

Iregenone Di- and Tri-carboxylic Acids, CH₂[4]C₂H₃ { [1]C(CH₃)₂CO₂H and CO₂H[4]C₆H₃ { [1]C(CH₃)₂CO₂H (B. 26, 2684).

MONO-NUCLEUS, AROMATIC SUBSTANCES, WITH UNSATU-RATED SIDE-CHAINS.

The benzene derivatives thus far considered contained saturated sidechains having carbon present in them. To these are attached the compounds having unsaturated side-chains—e. g.:

l'henylethylene, Styrolene, C₆H₅.CH:CH₂
Cinnamyl Alcohol, Styrone, C₆H₅.CH:CH.CH₂OH
Cinnamyl Aldehyde, . . . C₆H₅.CH:CH.CIO
Cinnamic Acid, C₆H₅.CH:CH.CO₂H
Acid, } C₆H₅C: C.CO₂H.

They can, like the unsaturated aliphatic bodies, be converted by numerous additive reactions into saturated compounds, as has frequently been shown in the preceding sections.

Ia. OLEFINE BENZENES.

Phenyl Ethylene, Styrolene, Vinylbenzene, C_6H_5 . CH: CH₁, boiling at 144°, occurs in storax (1–5 per cent.), from which it is obtained upon distillation with water. It also accompanies crude xylene in coaltar (B. 23, 3169, 3269). It is prepared (1) by the action of zinc-dust and glacial acetic acid upon phenylacetylene. Sodium and methyl alcohol will produce the same result (two hydrogen atoms are added) (B. 21, 1184). (2) By heating cinnamic acid with lime (B. 23, 3269) or with water to 200°. (3) By the action of alcoholic potash upon bromethyl benzene, and (4) by the condensation of acetylene, C_1H_1 , upon application of heat. (5) From vinyl bromide, benzene and aluminium chloride (A. 235, 331). (6) It is best obtained from β -brom-hydrocinnamic acid, which is immediately decomposed by a soda solution into styrolene, carbon dioxide and hydrobromic acid (B. 15, 1983). It is a mobile, strongly refracting liquid, with an agreeable odor. Pure styrolene is optically inactive; its sp. gr. = 0.925 at 0°.

Hydriodic acid converts styrolene into ethyl benzene, C_6H_5 . C_2H_5 ; hydrochloric and hydrobronic acids change it to a-haloid ethyl benzenes (B. 26, 1709), while with chlorine and bromine it yields a,β -dihaloid ethyl benzenes; chromic acid or nitric acid oxidizes it to benzoic acid.

With xylene and sulphuric acid, styrolene forms β -phenyl-a-tolyl propane; and with phenol, oxydiphenylethane (B. 24, 3889). Introsites, C₈H₅. C₂H₅. (N₂O₈) (B. 29, 356). Nitrous acid converts it into styrolene

A. Styrolenes containing the substituents in the side-group.—The derivatives of styrolene substituted in the vinyl residue will be discussed immediately after styrolene itself.

Two series of monosubstituted styrolenes result from the replacement of vinyl hydrogen. They are known as a- and ω -substitution products:

a-Bromstyrolene, CaH5CBr : CH9. ω-Bromstyrolene, C₆H₅. CH: CHBr.

The a-products result on heating styrolene chloride (-bromide) alone, with lime, or with alcoholic potash. They possess a penetrating odor, causing tears. They yield acetophenone (B. 14, 323) when they are heated with water (to 180°) or with sulphuric acid. a-Chlor-styrolene also results from acetophenone chloride (p. 189) when it is digested with alcoholic potash.

> a-Chlorstyrolene boils at 190°. a-Bromstyrolene " " 150-160° (75 mm.)

The ω -products are derived (along with phenylacetaldehyde) from the β -phenyla-chlor (brom.) lactic acids (p. 255), upon heating with water. ω-Chlorstyrolene is obtained also from ω-dichlor ethyl-benzene with alcoholic potash. ω-Bromstyrolene is formed from dibrom-hydrocinnamic acid (p. 255) by boiling with water. When they are heated with water, phenylacetaldehyde results. They are oils having a hyacinth-like odor.

See, further, phenylacetylene (p. 268) and phenylpropiolic acid (p. 284).

Dichlorstyrolene, C₆H₅. CCl: CHCl, boils at 221° (B. 10, 533).

Dibromstyrolene boils at 253° (B. 17, R. 22).

Di-iodstyrolene, phenylacetylene di-iodide, meltsing at 76°, is obtained from phenylacetylene and iodine (B. 26, R. 18). Tri-iod-styrolene, *Phenyl tri-iod-ethylene*, C₆H₅. CI: CI₂, melting at 108°, is obtained from phenyl iod-acetylene and iodine dissolved in CS₂ (B. 26, R. 19).

• Nitro-styrolene, phenylnitro-ethylene, C₆H₅. CH: CH(NO₂), melting at 58°, is obtained by boiling styrolene, with fuming sitisfication because with faming sitisfication.

obtained by boiling styrolene with fuming nitric acid, by heating benzaldehyde with nitromethane, CH₃(NO₂), and ZnCl₂ to 190° (B. 17, 527), and by the action of fuming nitric acid upon phenyl-isocrotonic acid (B. 17, 413), as well as by the action of NO₂ upon cinnamic acid, when the dinitro-compound, C₈H₅. C₂H₂(NO₂)₂. CO₂H, formed at first, decomposes (B. 18, 2438; 29, 357). It possesses a peculiar odor, provoking tears, is readily volatilized in aqueous vapor, and forms yellow needles. Dilute sulphuric acid decomposes it into harvaldshuda eacher monoids and hadronical decomposes it into benzaldehyde, carbon monoxide, and hydroxylamine.

Phenylnitropropylene, C_0H_5 . CH: $C(NO_2)CH_3$, melting at 63° , is obtained by the action of N_2O_3 upon phenylmethyl acrylic acid (B. 24, 2773). Phenylvinylamine, ω -Amidostyrolene, C_6H_5 . CH: CHNH₂, is very unstable. It is obtained by heating α -amidocinnamic acid (p. 276) (B. 17, 1622), and from ω -nitrostyro-

lene (B. 26, R. 677).

B. Styrolenes substituted in the benzene nucleus.—The three nitrostyrolenes are produced by the action of a cold soda solution upon the nitrophenylbrom-lactic acids (p. 255) or by boiling the β -lactones of the phenylbrom-lactic acids with water (B. 16, 2213; 17, 595).

o-, m-, p-Nitrostyrolenes, NO₂C₆H₄CH: CH₂, melt at +13°, -5° and +29°. o-Amidostyrolene is a very unstable, oily body. m-Amidostyrolene, boiling at 112-115° (12 mm.), is an oil, which polymerizes with ease. m-Azostyrolene melts at 38° (B. 26, R. 677). p-Amidostyrolene, melting at 81°, is formed on heating p-amidocinnamic acid, and together with p-amidocinnamic acid in the reduction of p-nitrocinnamic ester (B. 15, 1984).

C. Styrolenes substituted both in the benzene nucleus and in the sidechain.—PCl converts o- and p-nitroacetophenones into liquid ortho- and p-nitro-a-chlorstyrolene, NO₂. C₆H₄. CCl: CH₂, melting at 63° (A. 221,

o-Nitro-ω-chlorstyrolene, NO, . C₄H₄. CH: CHCl, melting at 58°, is obtained from o-nitrocinnamic acid and hypochlorous acid (B. 17,

o-Amido-chlorstyrolene, melting at 56°, yields indol when it is heated to 170° with sodium alcoholate; see also o-oxy-w chlorstyrolene (p. 269). p,w. Dinitrostyrolene melts at 199° (B. 17, R. 528).

Mention may be made of the following homologues of styrolene: m- and p-Methyl Styrolenes, CH, . C.H.CH: CH, boil at 1640 and

at 170-175° (B. 24, 1332).

Allyl Benzene, CaHa. CH: CH. CHa, boiling at 174°, is formed when styrone is reduced with hydriodic acid (B. 11, 670). Isoallylbenzene, Propenyl Benzene, C6H5. CH2. CH2. CH2, boiling at 155°, is obtained from benzene, allyl iodide, and zinc-

dust (A. 172, 132).

I b. Acetylene Benzenes; Phenylacetylene, Acetenyl Bensene, C₆H₅. C: CH, boiling at 139°, is produced (1) when a-brom-styrolene and (2) acetophenone chloride are heated to 130° with alcoholic potash; (3) also from phenyl propiolic acid (p. 284), on heating it with water to 120°, or upon distilling the barium or aniline salt (B. 29, R. 797).

It is a pleasant-smelling liquid. It forms metallic compounds, like acetylene, with ammoniacal silver and copper solutions: $(C_6H_5, C : C)_2$ Cu, is bright yellow, C_6H_5 . CH: CAg is white (B. 25, 1096). The sodium compound, C_8H_5 Na. inflames in the air, and with carbon dioxide it yields phenyl propiolic acid. When phenyl-acetylene is dissolved in sulphuric acid and diluted with water, it yields acetophenone, while styrolene is produced on boiling it with acetic acid and zinc-dust (B. 22, 1184).

Phenyliod-acetylene, C₆H₆C: CI, boils at 136° (22 mm.) (B. 26, R. 20)

o-Nitrophenyl Acetylene and p-Nitrophenyl Acetylene, $C_6H_4 < \frac{C}{NO_2}$, melting at 81-82° and 152°, are produced on boiling o-nitrophenylpropiolic acid and p-nitrophenylpropiolic acid with water.

o-Amidophenyl Acetylene, C6H4(NH2)C: CH, is an oil with an odor resembling that of the indigo vat. It is produced in the reduction of o-nitrophenyl-acetylene with zinc-dust and ammonia, or with ferrous sulphate and potassium hydroxide, and in the de-

composition of o-amidophenylpropiolic acid.

Phenylmethylacetylene, Phenylallylene, C₆H₅. C: C.CII₈, boiling at 185°, is produced on boiling phenylbrompropylene with alcoholic potash (B. 21, 276). Phenylethylacetylene, boiling at 201°, is obtained from sodium phenylacetylide and ethyl iodide, as well as from phenyliodacetylene and zinc ethide.

I c. Diolefine Benzenes.—p Divinylbenzene, CoH4(CH: CH2)2, is a liquid with an odor like that of petroleum. It is produced when p-di-a-bromethylbenzene is heated

with quinoline (B. 27, 2528).

II a. OLEFINE PHENOLS.

Various representatives of this class occur in the vegetable kingdom: chavicol, chavibetol, estragol, anethol, eugenol, safrol, asarone, apiol, etc. All are phenol-like derivatives of allyl- and isoallyl- or propenyl-The allyl fatty derivatives occurring in the vegetable kingdom were mustard oil (1, 423) and oil of garlic (1, 150).

A. Olefine Monoxybenzenes.—m-Vinylphenol, CH2: CII. C6H4. OII, boiling A. Olehne Monoxybenzenes.—m-vinyipnenoi, Ci₁₂: Cii. C₆Γ₄. Oli, boiling at 115° (16 mm.), is obtained from m-amidostyrolene (p. 267). o- and p-Vinyl anisols, CH₂: CH. C₆H₄. O. CH₃, boiling at 198° and 204°, have been obtained from the corresponding methoxycinnamic acids (B. 11, 515).
o-Oxy-ω-chlorstyrolene, HO. [2]C₆H₄. CH: CHCl, melting at 54°, is obtained from o-amido-ω-chlorstyrolene. Caustic potash converts it into cumarone (see this).
o-Thio-ω-chlorstyrolene, HS. C₆H₄. CH: CHCl; see benzothiophene.
Allyl- and Propenyl Phenols.—A very common property of the allyl phenols is their measurement induced by hot alcoholic rotats into isomeric propenyl com-

their rearrangement, induced by hot alcoholic potash, into isomeric propenyl compounds:

Methylchavicol, CH₂O.C₂H₄.CH₂.CH: CH₂---> CH₃O.C₂H₄.CH: CH.CH₃ Anethol. Metbyl Methyl Eugenol, (CH₂O)₂C₆H₂.CH₂.CH₃.CH₄.CH₅CH₅CH₅O)₂.C₆H₃.CH₅.CH₅CH₅. Isoeugenol Safrol, . . $(CH_2O_2)C_2H_2$. CH_2 . $CH_1: CH_2 \longrightarrow (CH_2O_2)$. C_6H_3 . $CH: CH.CH_3$ Isosafrol

$$\begin{array}{lll} \textbf{Apiol, . . .} & \begin{pmatrix} (\text{CH}_3\text{O})_2 \\ (\text{CH}_2\text{O}_2) \end{pmatrix} \cdot C_6\text{H.CH}_2 \cdot \text{CH:CH}_2 \cdot \text{CH:CH}_2 \cdot C_{(\text{CH}_3\text{O})_2} \\ \end{pmatrix} \cap_6 \text{H.CH:CH.CH}_3 & \text{Isoapiol.} \end{array}$$

The propenyl derivatives are distinguished from the allyl derivatives by higher specific gravities, higher melting points, and greater refractive power (B. 22, 2747; 23, 862). When the propenyl compounds are acted upon with nitrous acid, in glacial acetic acid, they yield di-isonitrososuperoxides, derivatives of a-diketones (see anethol). The allyland propenyl-phenols, when carefully oxidized with potassium permanganate, yield phenol glycols (p. 248) and phenol-glyoxylic acids (p. 259). See B. 29, 676, etc., for the action of bromine and alkalies.

Chavicol, p-Allyl Phenol, CH₂: CH. CH₂[4]C₆H₄OH, boils at 237° and occurs in the oil obtained from the leaves of Chavica Betle. It is a colorless oil with peculiar odor and its aqueous solution is colored blue by a drop of ferric chloride. Methyl Chav-

icol boils at 226°, and Ethyl Chavicol boils at 232° (B. 23, 862).

Estragol occurs in estragonal oil (B. 27, R. 46). It is isomeric with methyl chavicol. It boils at 215° (compare B. 29, 344). Both bodies change to anethol when heated with alcoholic potash. The cause of the isomerism of these two compounds has not yet been explained.

p-Anol, p-Propenyl Phenol, CH₃.CH: CH[4]C₆H₄OH, melting at 92°, is prepared

by heating anethol with caustic alkali (A. Suppl. 8, 88).

Anethol, p-Propenyl Anisol, CH₂. CH: CH[4]C₆H₄. O. CH₃, melting at 21° and boiling at 232°, occurs in anise oil, from the seed of *Pimpinella Anisum*, in that from the seed of *Illicium anisatum*, in the fruit of Anethum faniculum, and in estragonal oil. It is also formed from estragol and methyl chavicol (see above). It has been obtained synthetically from β -p-methoxyphenylmethacrylic acid; this would prove that its constitution is that of p-propenyl anisol (B. 10, 1604). Chromic acid oxidizes it to anisic and acetic acids, while dilute nitric acid changes it to anisic aldehyde (p. 219). Methoxyphenylglyoxylic acid is produced on treating it with potassium permanganate (p. 259). See also di isonitroso anethol peroxide, p. 250. o- and p-Propenyl Anisols boil at 222° and 227° (B. 29, R. 644).

B. Olefine Dioxybenzenes.—Of this group it is the olefine-3,4-dioxybenzenes which are almost exclusively known. They usually occur as ethers in plants, or are

obtained by the breaking down of plant acids.

Hesperetol, Vinyl-3,4-guaiacol, CH₃O[4] C₆H₃. CH: CH₃, melting at 57°, is produced in the dry distillation of calcium isoferulate (p. 283) (B. 14, 967).

Allyl-3,4-pyrocatechine is not known in a free condition. However, its three methyl ethers and its methylene ether have been found in ethereal oils.

Eugenol, Allyl-4,3 guaiacol, Eugenic Acid, HO[4] . CeH3. CH2. CH : CH3, is

an aromatic oil boiling at 247°. It is colored blue by ferric chloride. It occurs in the oil from Eugenia caryophyllata, in that from Eugenia pimenta, etc. Sodium amalgam reduces coniferyl alcohol to eugenol (p. 272) (B. 9, 418). Potassium permanganate oxidizes it to homovanillin, vanillin, and vanillinic acid. It breaks down into acetic acid and protocatechuic acid when fused with potassium hydroxide (p. 227). See B. 27, 2455; 28, 2082, for the derivatives of eugenol.

Chavibetol, Betel-phenol, Allyl-3,4-guaiacol, $_{\text{CH}_{3}\text{O}}^{\text{HO}[3]}$ C.H. CH. CH.

boiling at 254° (760 mm.), 131° (12 mm.), occurs in the ethereal oil obtained from the leaves of *Piper Betle* (J. pr. Ch. [2], 39, 349; B. 23, 862).

Eugenol Methyl Ether, *Allyl-3,4-veratrol*, (CH₂O)₂[3,4]C₈H₃. CH₂. CH: CH₃, boiling at 244°, is present in paracoto-oil (A. 271, 304), in the ethereal oil from *Asarum europeum* (B. 21, 1060), and in *baye-oil*. It has been synthetically prepared from pyro-oil. catechol dimethyl ether, allyl iodide, and zinc-dust (B. 28, R. 1055). Chromic acid oxidizes it to dimethyl protocatechuic acid or vetraric acid (p. 228). It forms isoeugenol methyl ether when heated with alcoholic potash. It also results when sodium eugenol or potassium chavibetol is treated with methyl iodide (J. pr. Ch. [2], 39, 353).

Safrol, Shikimol, Allyl-3,4-pyrocatechol methyleneether,

 $CH_2 < \begin{bmatrix} O[3] \\ O[4] \end{bmatrix}$ C₆H₃. CH₂. CH₃: CH₃, melting at 8° and boiling at 232°, is present in the oil of Sassafras officinalis, and in that of Illicium religiosum or Shikimino-Ki. Potassium permanganate oxidizes it to methylene-p-, m-dioxybenzylglycol (p. 248), homopiperonylic acid (p. 229), and piperonoyl carboxylic acid (p. 259), which are further oxidized to piperonal and piperonylic acid (p. 229) (B. 24, 3488; 28, 2088). Nitrosites (see B. 28, R. 1004).

Propenyl-3,4-pyrocatechol, isomeric with allyl-3,4-pyrocatechol, is not known in a free state. The propenyl pyrocatechol ethers: isoeugenol, isoeugenol methyl ether, and isosafrel, isomeric with the previously described allyl pyrocatechol ethers, are derived

from it.

Isoeugenol, CH₃O[3] C₆H₃CH: CH. CH₃, boiling at 260°, is formed when homo-

ferulic acid (p. 283) is distilled with lime and upon heating eugenol with caustic potash or sodium alcoholate in amyl alcohol (B. 27, 2580; Ch. C. 1897, I, 384).

Isoeugenol Methyl Ether, Propenyl-3,4-veratrol, boiling at 263°, results upon heating eugenol methyl ether with alcoholic potash (B. 23, 1165).

Potassium perman ganate oxidizes it to veratroyl carboxylic acid (p. 259) and veratric acid (B. 24, 2877).

It yields a glycol, melting at 88°, when it is carefully oxidized (p. 248).

Isosafrol, $CII_2 < \binom{O[3]}{O[4]} C_6II_3$. CH: CH. CH₃, boiling at 249°, is obtained from safrol by heating it with alcoholic potash, or with dry sodium ethylate. Potassium permanganate oxidizes it to a glycol (p. 248), melting at 101°, and piperonoyl carboxylic acid (p. 259). Chromic acid changes it to piperonal, artificial heliotropine (p. 220), from which it can be again reformed by condensation with propionic acid, and the splittingoff of CO, from the methylene-homo-caffetc acid, which is first produced (p. 283) (B. 29, R. 382). Sodium and alcohol reduce it to dihydrosafrol and m propyl phenol (B. 23, 1160).

C. Olefine Trioxybenzenes. - Asarone, Propenyl-2,4,5(?)-trimethoxybenzene, (CH₃O)₃[2,4,5]C₆H₂. CH: CH. CH₃, melting at 67° and boiling at 296°, separates from the ethereal oil of the root of Asarum curopeum, in which it is present together with terpenes and eugenol. Potassium permanganate oxidizes it to trimethoxybenzaldehyde and a trimethoxybenzoic acid (p. 231), which breaks down into CO, and oxyhydroqui-

none methyl ether when it is distilled with lime (B. 23, 2294).

Myristicine, Butenyl-3,4,5-trioxybensene methyl methylene ether,

(CH₂O₂) C₆H₂C₄H₇, melting at 30°, results upon treating the high-boiling portions of muscat nut oil and maci oil with metallic sodium. It can be oxidized to ethers of a trioxybenzaldehyde and a trioxybenzoic acid (B. 24, 3818).

D. Olefine Tetraoxybenzenes.—Apiol, Allylapionoldimethylmethylene ether, (CH₃-O)₂(CH₂O₂). C₆H. CH₂. CH: CH₂, melting at 30° and boiling at 294°, occurs in pars-

ley seeds and in Petroselinum sativum. Potassium permanganate oxidizes it to ethers of a tetraoxybenzaldehyde and a tetraoxybenzoic acid. See also apionol, p. 166. ing potash changes it to the isomeride isapiol, melting at 56° and boiling at 304° (B. 25, R. 908). An apiol, boiling at 162° (11 mm.), differing from the preceding only in the relative position of the methylene and methyl groups, occurs in the oil from Anethum graveolens (B. 29, 1800).

II b. Acetylene phenetol, CH: C. C₂H₄O. C₂H₅ (A. 269, 13).

III. PHENYLOLEFINE ALCOHOLS WITH THEIR OXIDATION PRODUCTS.

The chemistry of the phenylolefine alcohols, aldehydes, and ketones has not been fully developed. Their phenol-like derivatives will be discussed in immediate connection with the most important representatives of the class. The division in detail of the material into polyalcohols and their oxidation products, as was carried out with uni-nucleus benzene derivatives having oxygen-containing side-chains, is not feasible with uni-nucleus benzene derivatives having unsaturated oxygen-containing side-chains, because at present no representatives have been prepared for many classes of compounds which can be deduced theoretically. bodies belonging here will, therefore, be introduced at the proper places in connection with the simple phenylolefine alcohols and their oxidation products.

1 (a). Phenylolefine Alcohols.

The two phenylvinyl alcohols possible theoretically are not known, and apparently are incapable of existence. The a-haloid styrenes become acetophenone upon replacing their halogen atom by hydroxyl, while the β -haloid styrenes yield phenyl acetaldehyde:

a-Chlorstyrene,
$$C_6H_5$$
. CCl: CH₂ $\xrightarrow{H_2O}$ $\xrightarrow{}$ C_6H_6 . CO. CH₃ Acetophenone
ω-Bromstyrene, C_6H_6 . CH: CHBr $\xrightarrow{}$ C_6H_6 . CH₂. CHO Phenylacetaldehyde.

However, the corresponding ethyl ethers have been prepared:

β-Phenylvinyl-ethyl Ether, C₆H₅. CH: CH: C: C: C: H₅, boiling at 217°, is formed from ω-chlorstyrene (p. 267) and sodium ethylate (B. 14, 1868). a-Phenylvinylethyl Ether, C₆H₅C(OC₂H₅): CH₃, boiling at 209°, is obtained by splitting off alcohol from acetophenone acetal (p. 189) with heat, and is rearranged by heating under pressure into isomeric phenyl ethyl ketone (p. 189) (B. 29, 2931).

Styrone, Cinnamyl Alcohol, γ-Phenyl-allyl Alcohol, C₆H₅. CH: CH: CH₂OH, Phenyl-allyl Alcohol, C₆H₅. CH: CH: CH₂OH, Colored and Diling at 250°, occurs at cinnamic ester in limit.

melting at 33° and boiling at 250°, occurs as cinnamic ester in liquid Storax, the sap of the Liquidambar orientalis tree, found in the southwestern portion of Asia Minor. When oxidized it becomes cinnamic aldehyde, cinnamic acid, and benzoic acid; see also stycerine, p. 248. Styrylamine, CaH. CH: CH: CH, NH2, boils at 236° (B. **26**, 1858).

1 (b). Oxyphenylolefine Alcohols.

Oxyphenylvinyl alcohols are not known, but cumarone, C₆H₄ { [1]CH: CH | 2]O_____!, an inner anhydride, the cyclic ether of o-oxyphenylvinyl alcohol, has been made. It will be described later under the heterocyclic compounds.

Glyco-o-cumar-Alcohol, C₆H₁₁O₅.O.C₆H₄.CH:CH.CH₂OH, melting at 115°, has been formed from glyco-o-cumaraldehyde (see below).

Sec. Methyl-o-cumar-Alcohol, HO.C₆H₄.CH:CH.CH(OH)CH₃, melts at 47°. See methyl-o-cumar-ketone, p. 272.

HO[4] C_6H_3 . CH: CH. CH₄OH, Coniferyl Alcohol, m. Meliesy-p-esystyra CH₂O[3]

meking at 73°, is formed from coniferine (see this), which emulsin decomposes into glucoses and conferyl alcohol. Vanilline results from its oxidation (p. 219) and eugenol from its reduction (p. 270).

Cubebine, CH, (1/3), CeH, CH: CH. CH, OH, melting at 125°, is found in callebs, the fruit of Piper subsba.

2 (2). Phenylolefine Aldehydes.

Cinnamic Aldehyde, 3. Phenylacrolein, C.H., CH: CH. CHO, boiling at 247°, forms the chief constituent of cinnamon oil from Persea cinnamonum, and the oil from Perica Cassia, from which it can be extracted with acid sodium sulphite. The first product is the double derivative, C_6H_6 . CH: CH: CH: CH(OH)SO₃K, which combines with a second molecule of mono-potassium sulphite to yield C_6H_6 . CHSO₃K. CH₂. CH(OH). SO₃K + 2H₂O, which dissolves with difficulty (B. 24, 1805). The aldehyde results from the oxidation of cinnamyl alcohol, in the dry distillation of a mixture of the lime salts of cinnamic and formic acids, and by the action of hydrochloric acid gas or sodium hydrate (B. 17, 2117), or sodium ethylate (B. 20, 657) upon a mixture of benzaldehyde and acetaldehyde.

Cinnamic aldehyde is a colorless, aromatic oil, which distils readily in aqueous vapor. When exposed to the air it oxidizes to cinnamic acid. It adds chlorine and bromine very The dihaloid addition products change with ease into a-Mono-chlor- and readily. 1-Monobromcinnamic Aldehydes, CaHs. CH: CX. CHO, melting at 35° and 72°

(B. 24, 246).

a and 3 Trithiocinnamic Aldehyde melt at 167° and 213° (B. 24, 1452).

Hydro-cinnamide, (C,H,\2N, melts at 106°. Its phiny/hydracone, CeH5. CH: CH. CH(N,H. CeH5), melts at 168°. The symoxime melts at 138.5°.

The anti-exime, melting at 64°, is converted by hydrochloric acid gas in ethereal solution into the syn-oxime (B. 27, 3428). Isoquinoline is produced when the latter is heated with P₂O₅ (B. 27, 2795).

Nitrocinnamic Aldehydes are obtained from the aldehydes of the nitrophenyllactic acids (p. 248). o-, m-, and p-Nitrocinnamic aldehydes melt at 127°, 116°, and 141° (B. 18, 2335).

a-Methylcinnamic Aldehyde, C₆H₅. CH: C(CH₃)CHO (B. 19, 526, 1248).

2 (b). Oxyphenylolefine Aldehydes.

o-Cumaric Aldehyde, HO[2]C₆H₄, CH: CH. CHO, melting at 133°, is produced by the action of emulsin upon Glyco-o-cumaric aldehyde, C₈H₁₁O₈, O. C₆H₄, CH: CH: CHO, melting at 190°, the condensation product of helicine (see this) and acetaldehyde (B. 20, 1931). It occurs as methyl ether in the oil of cassia (B. 28, R. 386). m- and p-Acrylaldehydophenoxyl-acetic Acid, CO₂H. CH₂O. C₆H₄. CH: CH. CHO (B. 19, 3049).

Piperonyl Acrolein, (CH₂O₂)[3.4]C₆H₃CH: CH . CHO, melting at 70°, is obtained from piperonal, acetaldehyde, and sodium hydroxide (B. 27, 2958); see piperic acid.

Phenyldiolefine Aldehydes.

o Nitrocinnamenyl Acrolein, NO₂C₆II₄. CH: CH: CH: CH: CHO, melts at 153° (B. 17, 2026).

4 (a). Phenylolefine Ketones.

The phenylolefine ketones are readily obtained from the corresponding

aldehydes and methyl ketones by means of sodium hydroxide.

Benzal Acetone, Benzylidene Acetone, Cinnamyl Methyl Ketone, C₆H₆. CH: CH. CO. CH₃, melting at 41° and boiling at 262°, is produced in the distillation of calcium cinnamate and acetate, as well as in the condensation of benzaldehyde and acetone with dilute sodium hydroxide (A. 223, 139).

It dissolves with an orange-red color in sulphuric acid. Its phenylhydrazone, melting at 156°, readily rearranges itself to 1,6-diphenyl-3-methylpyrazoline and 1,5-diphenyl-3-pyrazole (see this) (B. 20, 1099). Its oxime melts at 115° (B. 20, 923). Boiling sodium hypochlorite converts benzalacetone into cinnamic acid. Chloroform is eliminated at the same time. The nitration of benzalacetone produces the o- and p-nitro-Benzalacetone and sodium malonic ester condense to phenyldihydroresorcylic ester (B. 27, 2054, 2199).

o- and p-Nitrobenzal Acetone melt at 60° and 110°, respectively (p. 249). The o-body passes readily into indigo. a-Methyl-quinoline results from it by reduction.

Water is simultaneously liberated.

Piperonylidene Acetone, (CH₂O₂)C₆H₃CH: CH. CO. CH₃, melts at 96° (B. 28,

R. 1009).

Cuminol Acetone (A. 223, 147). Allyl Acetophenone, C₆H₅. CO. CH₂.-CH₂.CH₃. CH₃ crom allyl benzoyl acetic acid (B. 16, 2132), boils at 236°.

4 (b). Oxyphenylolefine Ketones.

o-Oxybenzal Acetone, Methyl-o-cumar-ketone, HO . C6H4 . CH : CH . CO . CH3, melting at 139°, is obtained from salicylaldehyde, and also by the action of emulsin **The latter compound is a condensation product of helicine (see this) and acetone** (B. 24, 3180). o-, m-, and p-Phenoxyacetic acid-acryl methyl ketones melt at 108°, 122°, and 177° (B. 19, 3056).

5. Phenyldiolefine Ketones.
Cinnamenyl Acetone, C₆H₅. CH: CH: CH: CH: CO: CH₃, melting at 68°, results from the condensation of cinnamic aldehyde and acetone. Its oxime yields a pyridine derivative upon dry distillation (B. 29, 613). Benzalmesityl Oxide, C₄H₅. CH: CH. CO. CH: C(CH₃)₂, boils at 178° (14 mm.) (B. 14, 351). Piperonylene Acetone, (CH₂O₂)C₆H₅. CH: CH. CH: CH. CO. CH₃, melts at 89° (B. 28, 1193).

6. Phenylolefine Carboxylic Acids.

These acids arrange themselves into two distinct classes. class is derived from a saturated acid by substituting an unsaturated sidechain for hydrogen attached to the benzene nucleus—e. g., vinyl benzoic acid. The second class comprises the phenylated olefine monocarboxylic acids.

A. Phenylolefine Carboxylic Acids having their CO₂H group attached to the nucleus.

o-Vinyl Benzoic Acid, CH₂: CH[2]C₈H₄. CO₂H. o-Vinyl benzoic acids, chlorinated in the vinyl residue and also in the benzene residue, have been obtained by the decomposition of chlorinated hydrindene and naphthoquinone derivatives (B. 27, 2761; A. 275, 347). m Vinyl Benzoic Acid, melting at 95°, is formed from m amidoo. Vinylphenyl Acetic Acid, CH₂: CH C₂II₄. CO₂H. Derivatives of this acid, chlorinated in the visyl residue, have also been obtained by the breaking-down of

chlorinated ketohydronaphthalenes (B. 21, 3555).

B. Phenylolefine Carboxylic Acids with the carboxyl group in

the unsaturated aliphatic side-chain.

The true phenylolesine monocarboxylic acids may be obtained by the oxidation of corresponding alcohols and aldehydes, as well as by similar methods from the phenylparaffin monocarboxylic acids or fatty acids (1, 277). The nucleus-synthetic method, however, is far more important; it consists in the action of the sodium salt and the anhydride of a fatty acid upon an aromatic aldehyde (Perkin's reaction).

History.—As early as the year 1856 Bertagnini found that cinnamic acid was formed upon heating benzaldehyde with acetyl chloride. In 1865 W. H. Perkin, Sr., synthesized coumarin, the lactone of o-oxycinnamic acid (p. 281), by heating sodium salicylaldehyde with acetic anhydride. In 1875 Perkin gave this reaction an entirely different aspect by allowing sodium acetate and acetic anhydride to act upon salicylaldehyde. In this modified form the reaction acquired more general application.

Many chemists have assisted in the amplification of the Perkin reaction, which in

consequence has become one of the most fruitful synthetic methods.

The course of the reaction has been made clear by the researches of v. Baeyer and O. R. Jackson, Conrad and Bischoff, Oglialoro, and especially by those of Fittig and his students, Jayne and Slocum (A. 215, 97, 116; 227, 48):

(1) In the condensation of aromatic aldehydes and fatty acids the carbon atom, com-

bined with the carboxyl group, unites with the carbon of the aldehyde group.

(2) The reaction takes place with the aldehyde and the sodium salt of the fatty acid.

The anhydride of the latter acts as a dehydrating agent.

(3) The condensation proceeds in two stages: (a) the union of the aldehyde and the sodium salt, as in the formation of aldol, with the production of the sodium salt of a β -oxyacid; (b) the exit of water from the β -oxyacid, resulting in the formation of the olefine carboxylic acid. In many instances the reaction was arrested in the first stage:

(a)
$$C_6H_5$$
. $CHO + CH_2$. $CO_2Na \xrightarrow{-H_2O} C_8H_5$. $CH(OH)$. CH_2 . CO_2Na .
(b) C_6H_5 . $CH(OH)CH_2$. $CO_2Na \xrightarrow{-H_2O} C_8H_5$. $CH: CH$. CO_2Na .

A second nucleus-synthetic method for the preparation of phenyl-olefine carboxylic acids consists in the condensation of benzaldehydes with fatty acid esters by means of sodium ethylate or metallic sodium (Claisen, B. 23, 976):

$$C_6H_5$$
. CHO + CH₃. CO . O . $C_2H_5 \xrightarrow{-H_2O} C_6H_5$. CH : CH . CO₂ . C_2H_5 .

Phenyl Acrylic Acids.—According to the structural theory, there are two possible isomerides, the α - and β -acids, which are known in cinnamic and atropic acids:

From what was learned in connection with the alkyl acrylic acids we might well expect the existence of one unstable (labile) modification of cinnamic acid. However, not less than three unstable (labile) forms of the ordinary cinnamic acid (p. 276) have been observed: two among the alkaloids occurring in the synthesis of cocaine—natural iso-cinnamic acid and allo-cinnamic acid (Liebermann). The third variety is the artificial iso-cinnamic acid (Erlenmeyer, Sr., A. 287, I) formed in the reduction from alcoholic solution of the unstable (labile) a bromeinnamic acid (the β -bromeinnamic acid of Glaser) with zinc-dust.

Cinnamic Acid, β-Phenyl Acrylic Acid, Acidum cinnamylicum, C₆H₅. CH: CH. CO₂H, melting at 133° and boiling at 300°, occurs in Peru and tolu balsams, in storax, and in some benzoin resins; also, together with a- and β -truxillic acids, the natural isocinnamic and allocinnamic acids, in the decomposition products of the associated alkaloids of cocaine.

Formation.—It is produced (1) by the oxidation of its alcohol and its aldehyde; (2) by the reduction of phenylpropiolic acid with zinc-dust and glacial acetic acid (B. 22, 1181); (3) nucleus-synthesis—from benzal-dehyde: (a) with sodium acetate and acetic anhydride, (b) with acetic ester and sodium ethylate (see above); (4) upon heating benzal chloride The latter reaction serves for the technical prepawith sodium acetate. ration of cinnamic acid (B. 15, 969); (5) by heating benzalmalonic acid (p. 288); (6) its phenyl ester is produced when phenyl fumaric ester is heated (p. 148).

Properties and Deportment.—Cinnamic acid crystallizes from hot water in fine needles, from alcohol in thick prisms. It is soluble in 3500 parts of water of 17°, and readily in hot water. It may be purified by distillation under greatly reduced pressure, or by crystallization from petroleum benzine (A. 188, 194).

Ferric chloride produces a yellow precipitate in solutions of the cinnamates.

Nitric acid and chromic acid oxidize it to benzaldehyde and benzoic acid. It is converted into phenylglyceric acid by potassium permanganate (p. 255). Fusion with

caustic potash decomposes it into benzoic and acetic acids.

Being an unsaturated acid, cinnamic acid can readily take up hydrogen, hydrogen bromide, hydrogen iodide, bromine, chlorine, and hypochlorous acid, with the production of hydrocinnamic acid (p. 197), β -brom-, β -iodhydrocinnamic acid (p. 255), phenyl- a,β dichlor-, a,β-dibrompropionic acid or cinnamic acid dichloride, cinnamic acid dibromide, and β -phenyl- α -chloriactic acid (p. 255).

Cinnamic Acid Derivatives .- Methyl Ester melts at 33° and boils at 263°. Ethyl Ester boils at 271°. Phenyl Ester melts at 72° and boils at 206° (15 mm.); see cinnamic acid. Pyrocatechol Ester melts at 129° (B. 11, 1220; 18, 1945; 25, 3533). Styryl Ester, Styracine, melts at 14°. The chloride melts at 35° and boils at 154°. (25 mm.). The anhydride melts at 130° (B. 27, 284). The amide melts at 141°. The anilide melts at 151°. The nitrile melts at 11° and boils at 254° (B. 15, 2544; 27, R. 262).

Haloid Cinnamic Acids Substituted in the Side-chain.—(a) Phenyl monohaloid Acrylic Acids. The structural theory provides for two isomeric monochlor-acrylic acids, but there are really two modifications for each of these structural isomerides. tomary to distinguish them as a- and β -chlorcinnamic acid and allo- α - and allo- β -chlor-

cinnamic acid (B. 22, R. 741; A. 287, 1).

a-Chlorcinnamic Acid, C₆H₅. CH: CCl. CO₂H, melting at 137°, is formed (1) by the action of alcoholic potash on phenyl-a-, \(\beta\)-dichlorpropionic acid; (2) from benzaldehyde, sodium monochloracetate, and acetic anhydride; (3) from phenyl-a-chlorlactic acid by means of acetic anhydride and sodium acetate; (4) by the action of CrO, upon aldehyde (B. 24, 249).

Allo-a-chlorcinnamic Acid, melting at 111°, is produced, together with a-chlorcin-

namic acid, according to method 1.

β-Chlorcinnamic Acid, C₆H₅. CCl: CH. CO₂H, melting at 132.5°, and Allo-β-chlorcinnamic Acid, melting at 142°, are formed by the addition of hydrochloric acid

to phenylpropiolic acid.

a-Brom-cinnamic Acid, CaH. CH: CBr. COaH, melting at 130°, and Allo-abrom-cinnamic Acid, melting at 120° (Glaser's β -brom-cinnamic acid), result when phenyl-a, \beta-dibrompropionic acid is acted upon with alcoholic potash. The latter, when beated, changes to the higher-melting a-brom-cinnamic acid. When it is treated with zinc dust in alcoholic solution it yields "artificial isocinnamic acid," together with allocinnamic acid. The latter, very probably, is the primary product of the reaction, and is converted by the zinc bromide into the artificial isocinnamic acid. Both yield benzaldehyde upon oxidation.

 β -Brom-cinnamic Acid, C_8H_5 . CBr: CH. CO₂H, melting at 133°, and Allo- β -brom-cinnamic Acid, melting at 158.5°, are formed simultaneously upon the addition of hydrogen bromide to phenylpropiolic acid. The second acid, upon heating, changes to the lower-melting β -brom-cinnamic acid, and upon reduction yields not only cinnamic

acid, but also "artificial isocinnamic acid."

(b) Phenyldihaloid Acrylic Acids result from the addition of halogens to phenylpropiolic acid. Dichlorcinnamic Acid, C₄II₅. CCl: CCl. CO₂H, melts at 120° (B. 25, 2665). a- and β-Dibrom-cinnamic Acids melt at 139° and 100° (B. 25, 2665). Di-iodcinnamic Acid melts at 121° (B. 24, 4113).

The unstable (labile) modifications of Cinnamic Acid (p. 274):

Natural Isocinnamic Acid melts at 45-47° (57°), monoclinic (B. 23, 147).

Allo-cinnamic Acid melts at 66°, monoclinic (B. 27, 2048).

Artificial Isocinnamic Acid melts at 43.5-46°, monoclinic (A. 287, 7).

All the varieties crystallize in monoclinic forms, which show no relationship to one another. The ratio of axes and the magnitude of angles are entirely different. The crystals of the artificial isocinnamic acid are characterized by their remarkable decomposability, which disappears with the other (labile) modifications.

Cinnamic acid cannot be converted into any of its unstable (labile) modifications. Allo-cinnamic acid forms an aniline salt, melting at 83° and dissolving with difficulty in It can also be easily obtained from the natural and the artificial isocinligroine.

namic acid.

Thus far "natural isocinnamic acid," has only been found in the decomposition acids of the alkaloids associated with cocaine, where it occurs together with ordinary and allocinnamic acids. The allo-cinnamic acid, however, has also been obtained with much cinnamic acid from benzalmalonic acid, and together with "artificial isocimnamic acid" by reducing allo-a- and allo-a-brom-cinnamic acid in alcoholic solution, as well as from both isocinnamic acids by means of aniline. When allo-cinnamic acid is treated with zinc and bromine in alcoholic solution it yields artificial isocinnamic acid. Chlorine and bromine convert it into allo-cinnamic acid dichloride and allo-cinnamic acid dibromide (p. 255), addition products, differing from cinnamic acid dichloride and cinnamic acid dibromide. Concentrated sulphuric acid converts the three unstable (labile) modifications into ordinary cinnamic acid.

When a benzene solution of allo-cinnamic acid is exposed to sunlight the allo-acid gradually changes to the ordinary cinnamic acid. The addition of a trace of iodine ac-

celerates this transposition very materially (B. 28, 1446).

The "natural isocinnamic acid" also changes to the ordinary cinnamic acid under the influence of small quantities of iodine, by exposure to sunlight, or upon boiling and by heating with water to 260° (B. 23, 516).

Four polymeric dicinnamic acids have been discovered in the isomeric truxillic acids

It is very probable that they are diphenyltetramethylene dicarboxylic acids.

a Amidocinnamic Acid, C₆H₅. CH: C(NH₂). CO₂H, decomposes, when rapidly Its hydrochloride is heated, at 240-250°, with the production of phenylvinylamine. produced upon heating its benzoyl-lactimide with hydrochloric acid to 120°. The acid itself may be liberated from the hydrochloride by means of sodium acetate or soda.

a Acetamido-cinnamic Acid, Calls, CII: C(NHCO, CH3), COaH + 2H,O, melts, when anhydrous, at 190° with decomposition. It is formed when sodium hydroxide acts upon acetlactimide. The amide of an isomeric (?) a-amidocinnamic acid, melting at 100°, results when ammonia acts upon phenyldibrompropionic acid ester or a-brom-cinnamic acid ester (B. 29, R. 795).

a-Acetamido-cinnam-lactimide, C₆H₅. CH: CONCOCH₅, melting at 146°, relies from the action of continuous states and the section of continuous states are section of continuous states and the section of continuous states are section of continuous states and the section of continuous states are sults from the action of acetic anhydride upon a-amidophenyl-lactic acid, and from glycocoll, benzaldehyde, sodium acetate, and acetic anhydride.

a Benzoylamido-cinnam-lactimide, $C_{6}H_{5}$. CH: C > N. CO. $C_{6}H_{5}$, melts at 165°. It is produced in the condensation of hippuric acid and benzaldehyde with acetic anhydride and sodium acetate. See phenylpyroracemic acid (p. 259). When heated with dilute alkalies the lactimide changes to a-benzoyl-amido-cinnamic acid, which decomposes at 275° with the formation of phenylacetaldehyde (A. 275, I; 284, 36).

CO

Cinnamic Acids substituted in the benzene nucleus are isomeric with the

corresponding monocinnamic acid derivatives, having side-chain substitutions.

I. Monohaloid-cinnamic acids have been made from the three nitro-cinnamic acids as starting-out substances (B. 16, 2040; 18, 961; 25, 2109).

o-, m-, and p-Chlor-cinnamic Acids melt at 2000, 1760, and 2410.

o and m Brom-cinnamic Acids melt at 212° and 178°.

o-, m-, and p-Iod-cinnamic Acids melt at 213°, 181°, and 255°.

2. Nitro-cinnamic Acids.—The introduction of cinnamic acid into nitric acid of specific gravity 1.5 leads to the formation of the ortho- (60 per cent.) and para-nitro acids. To separate them, cover the acid mixture with 8-10 parts of absolute alcohol, and conduct hydrochloric acid gas rapidly into the liquid, until complete solution ensues.

On cooling, the para-ester separates. The pure esters are saponified with sodium carbonate or with dilute sulphuric acid, when the pure acids result (A. 212, 122, 150; 221,

265).

The three isomeric acids can be prepared from the corresponding nitro-benzaldehydes

by means of the Perkin's reaction:

o-, m-, and p-Nitro-cinnamic Acids melt at 240°, 197°, and 286°. o-, m-, and p-Nitro-cinnamic Ethyl Esters melt at 44°, 78°, and 138°.

Oxidation converts the three nitro-cinnamic acids into the three nitrobenzaldehydes (p. 186) and nitrobenzoic acids (p. 210). Bromine unites with o- and p-nitrocinnamic acids and their esters; see p. 255 and nitrophenylpropiolic acids.

3. Amido-cinnamic Acids can be prepared by reducing the three mononitrocinnamic acids with tin and hydrochloric acid. The reduction is better effected with ferrous sul-

phate in an alkaline solution (B. 15, 2294; A. 221, 266).
o-, m-, and p-Amido-cinnamic Acids melt at 158°, 181°, and 176°. When the diazo-bodies are boiled with haloid acids the haloid cinnamic acids, described above, are produced; but when they are acted upon with boiling water, the products are o-, m-, and

p-coumaric acids (pp. 280, 282).

Derivatives of o-Amido-cinnamic Acid.—The ethyl ester is obtained by reducing o-nitro-cinnamic ester with tin and hydrochloric acid in alcoholic solution (B. 15, 1422).

It separates in fine yellow needles, melting at 77°.

o-Ethyl Amido-cinnamic Acid, $C_6H_4 < \frac{CH : CH : CO_2H}{NH : C_2H_5}$, is obtained when ethyl iodide and potassium hydroxide act upon o-amido-cinnamic acid (B. 15, 1423). It melts at 125°.

Benzoyl-o amido-cinnamic Acid, C₆H₅. CO. NH. C₆H₄. CH: CH: CO₂H, melting at 192°, results from the oxidation of N-benzoyltetrahydroquinaldine (B. 25, 1263).

Carbostyril Formation.—Free o-amido-cinnamic acid differs from o-amidohydrocinnamic acid in deportment, in that when heated alone it does not give rise to an inner an-hydride formation; it behaves like o coumaric acid. The anhydride formation occurs, however, when o-amidocinnamic acid is heated with hydrochloric acid (B. 13, 2070), or with 50 per cent. sulphuric acid (B. 18, 2395). The resulting anhydride is carbostyril, discovered in 1852 by Chiozza, when he reduced o-nitrocinnamic acid with ammonium sulphide. It can be viewed both as a lactime and a lactam:

According to the second formula, carbostyril is nothing more than a-oxyquinoline; hence it will be discussed later, in conjunction with quinoline. This will also be done with the alkyl compounds derived from both formulas.

4. o-Nitrosoethylamido-cinnamic Acid, NO. N(C₂H₅). C₈H₄CH: CH. CO₂H, melts at 150°, with decomposition. It is obtained from o-ethyl-amido-cinnamic acid. When reduced it condenses to ethylisindazole-acetic acid (see this).

5. o-Hydrazine-cinnamic Acid, NH₂. NH. C_6H_4 . CH: CH. CO_2H , melts at 171°, with decomposition into indazole, $C_6H_4 < \begin{matrix} CH & NH \\ N-I \end{matrix}$ (see this), and acetic acid.

o-Sulphohydrazine-cinnamic acid, SO3H.NH.NH.C6H4CH:CH.CO2H, is formed when sodium sulphite acts upon the hydrochloride of o diazocinnamic acid. Hot hydrochloric acid breaks it down into o-hydrazine-cinnamic acid and the lactam of this acid, C₆H₄ { [1]CH: CH. CO, melting at 127° (A. 221, 274).

6. Sulpho-cinnamic acids are produced when fuming sulphuric acid acts upon cinnamic acid (A. 173, 8). The m-derivative has been obtained by a nucleus-synthesis from m-benzaldehyde-sulphonic acid (p. 187).

Cinnamic Acids Substituted both in the Side-chain and in the Bensene Nucleus .- aand β -Nitro-o-amido-cinnamic Acids, melting at 240° and 254°, have been prepared from o-amido-cinnamic acid. a,m-Dinitro-cinnamic Acid, $NO_2[3]C_6H_4$. CH: C-(NO₂)CO₂II, is formed when a mixture of nitric and sulphuric acids acts upon m-nitrocinnamic ester (A. 229, 224).

a,p-Dinitro-cinnamic Acid, p-Nitrophenyl-a-nitroacrylic acid, has been obtained from p-nitro cinnamic acid (A. 229, 224). Also consult ω , p-dinitrophenyl-ethylene (p. 267)

and p-amidophenylalanine (p. 254).

Homologous Cinnamic Acids.—Cinnamic acids containing alkyl groups in the benzene residue are produced when alkylized benzaldehydes are condensed with sodium acetate and acetic anhydride. The three tolyl aldehydes yield o-, m-, and p-methyl-cinnamic acids, β , o-, m-, and p-tolyl acrylic acids, melting at 169°, 115°, and 196°. Cuminol yields p-cumenyl-acrylic acid, (CH₃)₂CH[4]C₆H₄. CH: CH. CO₂H, melting at 158°. When the latter is nitrated it yields not only the p-nitro-acid, but also o-nitrocumenylacrylic acid, which manifests the same reaction transpositions as o-nitro-cinnamic acid (B. 19, 255).

a-Alkyl substituted cinnamic acids are produced in the condensation of benzaldehyde

with sodium propionate or butyrate and acetic anhydride (A. 227, 57).

a-Methyl Cinnamic Acid, a-Benzal-propionic Acid, β-Phenylmethacrylic Acid, C₆H₅. CII: C(CII₃)CO₂II, melting at 78° and boiling at 288°, is also formed from benzyl propionic ester and metallic sodium (see p. 192 and B. 20, 617). Phenyl-angelic Acid, a-Ethyl Cinnamic Acid, a-Benzal-n-butyric Acid, CaHa, CH: C(CaHa)COaH, melts at 104° (B. 23, 978).

Higher w-phenyl-n-olefine carboxylic acids are produced by heating the lactone carboxylic acids, when carbon dioxide is expelled, and in the reduction of phenyl diolefine

dicarboxylic acids.

Phenyl-iso-crotonic Acid, β-Benzal-propionic Acid, C. II. CH: CH: CH. CH. CO. H, melts at 86° and boils at 302° with partial decomposition into water and a-naphthol. It is formed also by expelling CO, and rearranging phenylparaconic acid, as well as from phenyltrimethylene tricarboxylic acid (B. 25, 1155) upon the application of heat. It unites with hydrogen bromide, forming \(\gamma \)-phenyl-\(\gamma \)-brombutyric acid, which yields phenylbutyro-lactone with a soda solution. Boiling dilute sulphuric acid converts it directly into phenylbutyrolactone (p. 254).

a. and β-Methylphenyl-iso crotonic Acids melt at 110° and 112° (A. 255, 262). Hydrocinnamenyl Acrylic Acid, C, H₅. CH₂. CH: CH. CH₄. CO, II, melting at 31°, is formed when sodium amalgam acts upon cinnamenyl acrylic acid (p. 285). The conversion of phenyl iso-crotonic acid and hydrocinnamenyl acrylic acid into isomeric acids by displacement of the double linkage, upon boiling them with sodium hydroxide (A.

283, 309), is worthy of note:

$$\begin{array}{c} \textbf{C_6H_5} \cdot \textbf{CH} : \textbf{CH} : \textbf{CH}_2 \cdot \textbf{CO_3H} & \longrightarrow \textbf{C_6H_6} \cdot \textbf{CH}_1 \cdot \textbf{CH} : \textbf{CH} \cdot \textbf{CO_3H} \\ & \textit{ap-Phenyl-crotonic Acid, m. p. 65°}, \\ \textbf{C_6H_5} \cdot \textbf{CH_2} \cdot \textbf{CH} : \textbf{CH} \cdot \textbf{CH_2} \cdot \textbf{CO_3H} & \longrightarrow \textbf{C_6H_6} \cdot \textbf{CH_3} \cdot \textbf{CH_2} \cdot \textbf{CH} : \textbf{CH} \cdot \textbf{CO_3H} \\ & \textit{ap-Phenylpropylidene Acetic Acid, m. p. 104°}. \end{array}$$

Atropic Acid, a-Phenylacrylic Acid, C₆H₅. C CO₂H, melts at 106°. This acid,

structurally isomeric with ordinary cinnamic acid, results from tropic acid and atrolactinic acid (p. 252) when they are heated with concentrated hydrochloric acid or with barytawater. It is sparingly soluble in cold water, easily in ether, carbon disulphide, and benzene, and distils with aqueous vapor. Chromic acid oxidizes it to benzoic acid; when fused with caustic alkali it yields formic and a-toluic acids; sodium amalgam converts it into hydro-atropic acid, and hydrochloric and hydrobromic acids change it to aand β -halogen hydro-atropic acids (p. 252).

Protracted fusion, or heating with water or hydrochloric acid, converts atropic acid to two polymeric isatropic acids, diatropic acids, (CallaO3)2 (melting at 237° and 206°), which bear the same relation to atropic acid that the truxillic acids sustain to cinnamic acid (B. 28, 137).

Methyl Atropic Acid, C₆H₅. CH. CH₃, melts at 135°, and is obtained from phenyl-acetic acid and paraldehyde by the action of acetic anhydride (B. 19, R. 251).

a-Phenyl-allyl-acetic Acid, C₆H₅. CH(CH₂. CH: CH₃)COOH, boiling at 200°, has been obtained from phenyl-allyl-malonic acid, and its nitrile from benzyl cyanide,

7. Oxyphenyl-olefine Carboxylic Acids.

allyl iodide, and caustic soda (B. 29, 2601).

A. Monoxyphenyl-olefine Carboxylic Acids.—Formation: They are obtained (1) from the corresponding amidophenyl-olefine carboxylic acids upon boiling the diazo-compounds with water (B. 14, 479); (2) by a nucleus-synthesis, when the phenol aldehydes are heated with the sodium salts and anhydrides of the fatty acids (Perkin's reaction, pp. 274, 278).

The following nucleus-syntheses (v. Pechmann) lead to the inner anhydrides or &-lactones of the o-oxycinnamic acids, the so-called coumarins: (3) the action of sulphuric acid upon phenol and malic acid, when it is very probable that the first product is the half-aldehyde of malonic acid, which condenses with the phenol.

(4) When sulphuric acid is allowed to act upon phenol and acetoacetic ester or mono-alkyl acetoacetic esters:

(3)
$$C_6H_4\begin{cases}H + CO_2H \cdot CH(OH) \cdot CH_3\\OH & HO CO\end{cases} \rightarrow C_6H_4\begin{cases}[1]CH : CH\\[2]O - CO\end{cases}$$
 Coumarin

(4) $C_6H_4\begin{cases}H + CH_3 \cdot CO \cdot CH_3\\OH C_2H_5O CO\end{cases} \rightarrow C_6H_4\begin{cases}[1]C(CH_3) : CH\\[2]O - CO\end{cases}$ coumarin.

The first members of this series are the monoxy-cinnamic acids, obtained by method \mathbf{r} from the three amido-cinnamic acids. o-Oxy-cinnamic acid or o-coumaric acid particularly is especially important. The δ -lactone *coumarin* corresponds to it. When coumarin is acted upon with bases, salts are formed which are isomeric with the o-coumarates. Isomeric dialkyl ethers are obtained from these isomeric salts.

The salts and ethers of coumarin are also designated as a-coumarates, and those of o-coumaric acid as the β -coumarates—salts and ethers. The cause of this isomerism is very probably dependent upon the fact that the lactone ring is still present in the salts and ethers of coumaric acid.

When the hydrogen atom in coumarin, occupying the o-position with reference to phenol-oxygen, is replaced by the nitro-group, free nitrocoumarinic acid may be liberated from the salts.

This acid is distinguished from free 3-nitro-coumaric acid in that by the exit of water it reverts to 3-nitrocoumarin. Both acids have corresponding dialkyl esters:

The cause of the difference in the ethers of o-coumaric and coumarinic acids whenever their structure was similar, has also been attributed to the different position of the atom groups in space:

This latter hypothesis, however, does not explain the varying deportment of the isomeric dimethyl ethers of 3-nitro-coumaric acid and 3-nitro-coumarinic acid. When 3-nitro-coumaric dimethyl ether is saponified with a soda solution the methyl ether-acid results; whereas 3-nitro-coumarinic dimethyl ether, under like treatment, yields 3-nitro-coumarinic acid. If the difference, with similar linkage relations, of the isomeric dimethyl ethers were solely due to spacial arrangement, then the varying behavior of the o-nitro-coumarinic dimethyl ester could be neither anticipated nor explained; whereas it would be obvious if the o-nitro-coumarinic dimethyl ester were regarded as a kind of carbonic acid ester (A. 254, 181):

$$\begin{split} &NO_{3}[3]C_{6}H_{3}\left\{ \begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CO}_{2}\cdot\mathrm{CH}_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right. \\ &NO_{3}[3]C_{6}H_{3}\left\{ \begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CO}_{2}H_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right. \\ &\longrightarrow NO_{2}C_{6}H_{3}\left\{ \begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CO}_{2}H_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right. \\ &\longrightarrow NO_{2}C_{6}H_{3}\left\{ \begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CO}_{2}H_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right. \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right] \right\} \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{OCH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH} \\ \mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \\ \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm{CH}_{3} \end{matrix} \right] \\ \\ &\longrightarrow \left[\begin{matrix} \mathrm{CH}:\mathrm{CH}\cdot\mathrm$$

Coumarin, its homologues and derivatives, will be arranged and treated as a group after o-coumaric acid.

o-Oxycinnamic Acid, o-Coumaric Acid, HO[2]C₆H₄CH:CH.-CO₂H, melting at 208°, and isomeric with hydrocoumarilic acid, phenyl-pyroracemic acid, etc., occurs in *Melilotus officinalis*, together with o hydro-coumaric acid, and in the leaves of *Angrecum fragans*. Nitrous acid converts o-amido-cinnamic acid into coumaric acid. It is most readily prepared by boiling coumarin for some time with concentrated potassium hydroxide, or, better, with sodium ethylate (B. 18, R. 28; 22, 1714). Its acetyl derivative is obtained from salicylic aldehyde and sodium acetate.

Ortho-coumaric acid is very easily soluble in hot water and in alcohol. It does not volatilize with steam. The free coumaric acid heated alone does not yield coumarin, but only when treated with acetic chloride or anhydride. Sodium amalgam converts it into melilotic acid, and fusion with potassium hydroxide into salicylic and acetic acids.

2-Methoxy-cinnamic Acid (β), CH₃O[2]C₈H₄[1]CH:CH.CO₂H, melting at 182°, is produced by the action of sodium acetate and acetic anhydride upon salicylaldehyde methyl ether, and by the rearrangement of methyl coumarinic acid (see this). Sodium amalgam reduces it to melilotic acid methyl ether, while bromine changes it to methyl-ether-dibrom-melilotic acid. o-Coumaric Dimethyl Ether (β), CH₂O[2]C₄· H₄[1]CH:CH:CO₂CH₃, boiling at 293°, is obtained from the previously described acid chloride by means of methyl alcohol. Acet-o-coumaric Acid, CH₃. CO:O[2]C₈H₄.

CH: CH.CO₂H, melting at 149°, is obtained from salicylaldehyde, acetic anhydride,

and sodium acetate (B. 20, 284); see commarin.

3-Nitro-commaric Acid (β), NO₂[3]C₈H₃[2](OH)CH: CH. CO₂H, is formed by the protracted heating of the dimethyl ether with sodium hydroxide. It suffers no change when heated with water, alcohol, or hydrogen bromide (distinction from 3-nitro-coumarinic acid). The *methyl ether-acid*, melting at 193°, is formed from 3-nitro-salicylaldehyde methyl ether, and from the *dimethyl ether*, melting at 88°, by the action of soda (see above). This latter ether is produced when methyl iodide acts upon the silver salt of the methyl ether-acid (B. 22, 1710).

Coumarin, C₆H₄ { [1]CH: CH | CO, melting at 67° and boiling at 290°,

occurs in Asperula odorata, in the Tonka beans (from Dipterix odorata), and in Melilotus officinalis. It is artificially prepared by heating acetoo-coumaric acid (B. 10, 287), the reaction-product, resulting from acetic anhydride and sodium salicylaldehyde (A. 147, 230), or from the action of acetic anhydride and sodium acetate upon salicylaldehyde (Perkin, Sr., B. 8, 1599). It has the agreeable odor of Asperula, and is applied in perfumery for the preparation of the Asperula essence.

Coumarin dissolves rather easily in hot water, and very readily in alcohol and in ether. It dissolves in caustic potash with a yellow color, the first product being potassium coumarinate, from which carbon dioxide separates coumarin. Boiling, concentrated caustic potash changes it to potassium coumarate. In aqueous solution it is reduced by sodium amalgam to melilotic acid (p. 226). When it is digested with an aqueous-alcoholic solution of potassium cyanide, hydrocyanic acid is added, and upon subsequent saponification o oxyphenylsuccinic acid is formed (A. 293, 366).

Coumarin Monomethyl Ester-acid, melting at 88°, and Coumarinic Dimethyl Ester, boiling at 275° (Constitution, p. 280), result when sodium coumarin is heated to 150° with methyl iodide. When heated both compounds change to the corresponding o-coumaric acid derivatives. The methyl ether-acid when exposed in alcoholic solution to sunlight also passes into the isomeric 2-methoxy-cinnamic acid. Coumaroxime, melting at 131° (B. 19, 1662), is produced when hydroxylamine acts upon thiocoumarin.

Coumarin Bromide, C₂H₂O₂Br₂, melting at 105°, is produced when bromine acts upon coumarin in carbon disulphide solution. Alcoholic potash converts it into a-brom-

coumarin, C_8H_4 $\left\{ \begin{bmatrix} 1 \end{bmatrix} CH : CBr \\ \begin{bmatrix} 2 \end{bmatrix} O - CO \right\}$ Boiling alcoholic potash changes both of these bodies

into coumarilic acid (see this). Thio-coumarin, C₆H₄ { [1]CH:CH [2]O—CS</sub>, melting at 101°, consists of golden-yellow needles. It is obtained from coumarin or o-coumaric acid by the action of P.S. (B. 19, 1661).

3-Nitro-coumarinic Acid, NO₂[3]C₆H₃ {[1]CH: CH [2]O—C(OH)₂(?), melts when rapidly heated, with the exit of water, at 150°, and passes on gentle warming with water or alcohol into the anhydride 3.nitro-coumarin, from which it is obtained upon boiling with soda. It forms long, yellow prisms. The silver salt and methyl iodide yield 3.nitrocoumarinic dimethyl ether, NO₂[3]C₈H₃ { [I]CH: CH [2]O—C(OCH₃)₂ (?) (Constitution, see p.

280).

Coumarin Homologues.—Following method 2, and using propionic, butyric and isovalerianic anhydrides, with their sodium salts, the products are a-alkyl coumarins. The β-alkyl coumarins are produced from phenols, acetoacetic ester, and sulphuric acid (B. 17, 2188) by method 4 (p. 279). P₂S₅ converts the a-alkyl coumarins into a-alkyl thio-coumarins (p. 281), which hydroxylamine changes to a alkyl coumarin oximes (p. 281) (B. 24, 3459). The melting points of the latter are given with those of the a-alkyl coumarins:

Dimethylamido-β-methyl Coumarin, melting at 143°, is obtained from dimethylamidous and acategorie actor (B. 22, 255)

amidophenol and acetoacetic ester (B. 30, 277).

m-Coumaric Acid, HO[3]C₄H₄. CH: CH: CO₂H, melting at 191°, has been formed from m-amido-cinnamic acid and from m-oxybenzaldehyde (B. 15, 2049, 2297).

Nitro-m-coumaric Acids, see B. 22, 292.

6-Amido-m-coumaric Acid has been obtained electrolytically from o-nitro-cin-

namic acid (B. 27, 1936).

p-Coumaric Acid, HO[4]C₆H₄. CH: CH: CO₉H, melting at 206°, is obtained from p-amido-cinnamic acid, and from p-oxybenzaldehyde; also on boiling the extract of aloes with sulphuric acid (Preparation, B. 20, 2528), and by the decomposition of the glucoside naringine (see this).

Methyl-p-coumaric Acid, from anisic aldehyde, melts at 154°. The phenol alkylethers of the coumaric acids yield ethers of unsaturated phenols (see o- and p-vinyl-anisol, p. 266), just as styrolene is obtained from β -bromhydrocinnamic acid, by the action of hydrogen bromide, and then a soda solution, when carbon dioxide is eliminated.

of hydrogen bromide, and then a soda solution, when carbon dioxide is eliminated.

B p-Methoxyphenylmethacrylic Acid, CH₂O[4]C₈H₄. CH: C(CH₂). COOH, melting at 154°, is obtained from anisic aldehyde and propionic acid. It breaks down,

when heated, into carbon dioxide and anethol (p. 269).

B. Dioxyphenyl-olefine Carboxylic Acids.—Caffeïc acid, or 3,4-dioxycinnamic acid, corresponding to protocatechuic acid (p. 227), and umbellic acid, or 2,4-dioxycinnamic acid, are the most important of the known dioxycinnamic acids, because they themselves, or their simple derivatives, occur in plants or appear as decomposition products of vegetable substances, and 3-methyl caffeïc acid, or ferulic acid, can be changed to the valuable vanillin (p. 219).

Caffeic Acid, β -,3,4-Dioxyphenylacrylic Acid, 3,4-Dioxycinnamic Acid, and its methyl- and methylene ether-acids, when reduced, become hydrocaffeic acid and its etheracids (p. 242). Oxidation yields protocatechuic acid and its ethers. When the acet-derivatives of the two methyl caffeic acids are oxidized with potassium permanganate the first products are the acet-derivatives of the two methyl-ether protocatechuic aldehydes. The caffeic acids and their ether-acids can be synthesized from protocatechuic aldehyde and its ethers with the aid of the Perkin reaction (p. 274). When fused with caustic potash caffeic acid and its ether-acids yield protocatechuic acid and acetic acid:

Caffeic acid is produced when coffee tannic acid is boiled with potassium hydroxide. It occurs in Cicuta virosa (B. 17, 1922). Ferric chloride produces a green coloration in

its solutions, which sodium carbonate changes to a dark red color.

Ferulic Acid, m-Methoxy-p-oxycinnamic Acid, occurs in the resin of Asafatida, and has been obtained from vanillin, as well as from m-methoxy-p-nitro-cinnamic acid, the product resulting from the action of nitric acid upon m-methoxycinnamic acid ether (B.

18, R. 682). Its acet-compound melts at 196°.

Isoferulic Acid, m-Oxy-p-methoxycinnamic Acid, Hesperitinic Acid, was first obtained from the glucoside hesperidine (see this). Both methyl ethers can also be prepared by a partial methylation of caffelc acid, when the chief product will be isoferulic

acid. Its acet-derivative melts at 199°.

Dimethyl Caffeïc Acid, (CH₃O)₂[3,4]C₆H₃. CH: CH. CO₂H, melts at 181° (B. 14,

Piperonyl Acrylic Acid, (CH₂O₂)[3,4]C₆H₂. CH: CH. CO₂H, melts at 232° (B.

13, 757).

Diacetcaffelc Acid, (CH₃CO₂)₂[3,4]C₆H₃. CH: CH. CO₂H, melts at 190° (B. 11, 686).

a-Homo-caffeïc Acid, 3,4-Dioxy-a-methyl Cinnamic Acid, melts at 193°. Its monomethyl ether-acid, Homoferulic Acid, (CH₂O)(OH)[3,4]C₆H₃.CH:C(CH₃).COOH, melting at 168°, yields isoeugenol when it is heated with lime (p. 270) (B. 15,

a-Hydropiperic Acid, (CH₂O₂)[3,4]C₄H₃CH₂. CH: CH. CH₂. CO₂H, melting at 78°, is formed when sodium amalgam acts upon piperic acid. When boiled with caustic soda it changes to β-Hydropiperic Acid, (CH₂O₂)[3,4]C₆H₃. CH₂. CH₃. CH₄. CH₄. CH₅. CO₂H, melting at 131°. Sodium amalgam converts the β -acid into piperhydronic acid, (CH₁O₂)[3,4]C₆H₂[CH₂]₄CO₂H, melting at 98°.

Umbellic Acid, 2,4-Dioxycinnamic Acid, (HO)₂[2,4]C₆H₂.CH:CH.CO₂H, decomposes about 240°. It is produced on boiling—

Umbelliferone, 4-Oxycoumarin, HO[4]C₈H₃ {[1]CH:CH | [2]O—CO, melting at 240°, with

caustic soda. It is found in the bark of Daphne mesereum, and is obtained by distilling different resins, such as galbanum and asafoetida. It is obtained synthetically from β -resorcyl aldehyde by method 2; and also by the condensation of resorcinol with malic acid according to method 3. It has an odor resembling that of coumarin, and behaves similarly with caustic potash. Its alkyl ethers show isomeric phenomena analogous to those developed under o-coumaric acid and coumarin (p. 281) (B. 19, 1778).

β-Methyl Umbelliferone, 4-Oxy-β-methylcoumarin, Resocyanine,

 $HO[4]C_8H_3$ ${1]C(CH_3): CH \atop [2]O----CO}$, melting at 185°, is formed when sulphuric acid acts upon

resorcinol and acetoacetic ester or acetylcyanacetic ester (B. 26, R. 314). See resacetophenone p. 221. a.,β-Dimethyl Umbelliferone melts at 256° (B. 16, 2127).

The corresponding bodies have been prepared from orcinol according to methods 3

and 4 (p. 279) (B. 17, 1649, 2188).

3. Oxycoumarin, melting at 280-285° with decomposition, and 5. Oxycoumarin, melting at 249°, are produced when pyrocatechol and hydroquinone are treated with

malic acid and sulphuric acid (B. 18, R. 333).

C. Trioxycinnamic Acids.—Inner anhydrides, δ-lactones of trioxycinnamic acids, are Daphnetin, 3,4-Dioxycoumarin, melting at 255°, and Æsculetin, 4,5: Dioxycoumarin, the aromatic decomposition products of the isomeric glucosides daphnin and æsculin. Æsculetinic and daphnetic acids are the trioxycinnamic acids corresponding to these dioxycoumarins. They are only known as ether-acids and ether-esters. permanganate oxidizes the triethyl ethers to triethoxybenzoic acids, which become triethoxybenzenes through the loss of carbon dioxide (B. 15, 2082; 17, 1086; 20, 1119).

D. Tetra-oxycinnamic Acids.—Fraxetin, melting at 227°, the aromatic decomposition product of the glucoside of fraxin (see this), contains the monomethyl ether of a trioxycoumarin. Isomerides of fraxetin have been prepared synthetically (B. 27, R.

130; 29, R. 293).

8. Phenylacetylene Carboxylic Acids.

Phenyl-propiolic acid, corresponding to propiolic acid, is important

because of its intimate connection with indigo and isatine.

Phenyl-propiolic Acid, C₆H₆. C: C.CO₂H, melting at 136°, is obtained by boiling α- and β-brom-cinnamic acids with alcoholic potash, by acting upon sodium phenyl-acetylene with carbon dioxide (1870, Glaser, A. 154, 140), and when the latter and sodium act upon ω-brom-styrolene. It is prepared by boiling the dibromide of ethyl cinnamate (p. 255) with alcoholic potash. When heated to 120° with water it decomposes into carbon dioxide and phenyl acetylene. It yields hydrocinnamic acid with sodium amalgam. Zinc-dust and glacial acetic acid, or sodium and methyl alcohol, convert it into cinnamic acid (B. 22, 1181).

Hydrogen chloride and bromide convert it into β-haloid- and allo-β-haloid cinnamic acids (p. 276). It combines with the halogens to phenyl-dihaloid acrylic acids, with hydrazine and phenylhydrazine to 3 phenyl-pyrazolon (see this) and 1,3-diphenylpyrazolon (B. 27, 783), and with sodium malonic ester to a tricarboxylic ester, which splits off carbon dioxide and becomes phenylglutaconic acid (p. 289) (B. 27, R. 163).

Ethyl Phenylpropiolic Ester, C₆H₆. C : C. CO₂C₂H₆, boiling at 260-270°, readily absorbs water and becomes benzoyl acetic ester (p. 259). Its *chloride* boils at 131° (25 mm.). Its *amide* melts at 102° (B. 25, 3537; 29, R. 795).

o-Nitro-phenyl Propiolic Acid decomposes at 156°. It is obtained when alcoholic potash acts upon the dibromide of o-nitro-cinnamic acid (Baeyer, A. 212, 140). When boiled with water it decomposes into carbon dioxide and o-nitro-phenyl acetylene. When boiled with alkalies it yields isatin.

It dissolves in concentrated sulphuric acid, with conversion into the isomeric isategenic acid, which at once forms carbon dioxide and isatin. Its silver salt explodes with

great violence when it is heated.

If digested with alkaline reducing agents (grape-sugar and potassium hydroxide, ferrous sulphate, hydrogen sulphide, potassium xanthate) it readily changes to indigo blue (Baeyer, 1880; B. 13, 2259).

Despite its comparatively high price, therefore, nitrophenyl propiolic acid is prepared technically, and serves as a substitute for natural indigo,

especially in calico printing.

The ethyl ester of the acid is obtained by conducting hydrochloric acid gas into the mixture of the acid and alcohol. It melts at 60-61°. When it is dissolved in sulphuric acid it changes to the isomeric isatogenic ester. Ammonium sulphide reduces it to the indoxylic ester (B. 14, 1741):

$$C_{6}H_{4} \begin{cases} [1]CO.C.CO_{2}C_{2}H_{5} \\ [2]N \stackrel{!}{\bigcirc} \\ \text{Isatogenic Ester} \end{cases} C_{6}H_{4} \begin{cases} [1]C : C.CO_{2}C_{2}H_{5} \\ [2]NO_{2} \\ \text{o-Nitrophenylpropiolic Ethyl Ester} \end{cases} C_{6}H_{4} \begin{cases} [1]C(OH) \\ [2]N - C.CO_{2}C_{2}H_{5} \\ \text{Indoxylic Ester}. \end{cases}$$

p-Nitro-phenyl Propiolic Acid, melting at 198°, is formed from the p-nitro-cinnamic ester after the same manner as the ortho-acid. When boiled with water it breaks up into carbon dioxide and p-nitrophenylacetylene. It yields p-nitroacetophenone if digested at 100° with sulphuric acid.

The ethyl ester, melting at 126°, when digested with sulphuric acid at 35°, forms p-

nitrobenzoyl acetic acid (p. 260).

1

o-Amido-phenyl Propiolic Acid melts at 129° with decomposition into CO₂ and o-amido-phenyl acetylene (p. 268). It is obtained by reducing o-nitrophenyl propiolic acid with ferrous sulphate and ammonia (B. 16, 679). It separates as a yellow, crystalline powder. When boiled with water it yields o-amido-acetophenone (p. 190).

γ-Chlorcarbostyril results when the acid is boiled with hydrochloric acid, and γ-οxycarbostyril upon heating it with sulphuric acid (B. 15, 2147):

$$C_{\mathbf{6}}H_{\mathbf{4}} \begin{cases} \text{CCI:CH} \\ \text{N} \end{cases} \text{C.OH} \underbrace{\overset{+ \text{ HCI}}{-H_{\mathbf{4}}O}} C_{\mathbf{6}}H_{\mathbf{4}} \begin{cases} \text{[I]C=C.CO}_{\mathbf{2}}H \\ \text{[2]NH}_{\mathbf{2}} \end{cases} \\ \text{C_{\mathbf{6}}}H_{\mathbf{4}} \begin{cases} \text{C(OH):CH} \\ \text{N} \end{cases} \text{COH.}$$

Sodium nitrite converts the hydrochloride into the diazo-chloride, which at 70° yields cinnoline-oxy-carboxylic acid.

m-Methylphenyl Propiolic Acid, CH₃[3]C₆H₄C : C.CO₂H, melts at 109° (B.

20, 1215).

9. Phenyldiolefine Carboxylic Acids have been prepared from cinnamic aldehyde by means of the Perkin reaction (p. 274). Cinnamenyl Acrylic Acid, C_6H_5 . CH:-CH: CH: CO₂H, melts at 165°. The nitrile, boiling at 285°, is obtained from cinnamenyl cyanacrylic acid (p. 289). The o- and p- nitro-acids, melting at 217° and 271°, were obtained from o- and p-nitrocinnamenyl acetone (p. 273) by the action of NaClO (A. 253, 356). The o-amido-acid melts with decomposition at 176° (B. 18, 2332). Cinnamenyl Crotonic Acid and Cinnamenyl Angelic Acid melt at 157° and

Piperic Acid, 3,4-Methylenedioxy-cinnamenyl Acrylic Acid, (CH₂O₂)[3,4]C₆H₃. CH: CH: CH: CO, H, melting at 217°, is produced, together with piperidine, when piperine is boiled with alcoholic potassium hydroxide. It can be synthesized by aid of the Perkin reaction from piperonylacrolein, and from piperonylene malonic acid (p. 289) (B. 28, 1190). Sodium amalgam converts it into two isomeric hydropiperic acids, a and B. It combines with four atoms of bromine. It is oxidized in dilute solution by potassium permanganate, at 0°, to piperonal and racemic acid (B. 23, 2372). When fused with potassium hydroxide it breaks down into acetic, oxalic, and protocatechuic acids. Its chloride and piperidine form piperine (see this).

History.—Fittig and Mielck (1874) determined the constitution of piperic acid.

Ladenburg and Scholtz (1894) effected its synthesis (B. 27, 2958).

a-Methyl- and a-Ethyl Piperic Acids, melting at 208° and 179°, were synthesized just like piperic acid (B. 28, 1187).

IV. COMPOUNDS WHICH MAY BE VIEWED AS OXIDATION PRODUCTS OF MONO-NUCLEUS, AROMATIC POLYALCOHOLS WITH UNSATURATED SIDE-CHAINS.

The domain of the aromatic polyalcohols having unsaturated side-chains has been even less completely and even more irregularly developed than that of the polyhydric, aromatic paraffin alcohols and their oxidation products. At present the alcohols and aldehydes are wholly lacking; from them the carboxylic acids and their derivatives belonging here can be theoretically deduced. Consequently the material in this section will not be sharply differentiated, although in the main the classification is the same as that observed with the oxidation products of the aromatic polyparaffin alcohols (pp. 232-266).

1. Phenylene Oxyolefine Carboxylic Acids.—Methylene phthalide and isocoumarin are inner anhydrides or lactones of the possible o-vinyl alcohol benzoic acids, not known

in a free state. Coumarin is isomeric with them.

Methylene Phthalide, C_0H_4 $\left\{ \begin{bmatrix} I \end{bmatrix}C = CH_1, \\ \begin{bmatrix} 2 \end{bmatrix}COO \right\}$, melting at 59°, is formed in the distillation of phthalyl acetic acid (p. 290). Its dibromide melts at 98°. Monobrom-methylphenone-carboxylic acid. Dichlor-methylene phthalide, C₈H₄ { [1]C = CCl₂ phenone-carboxylic acid. Dichlor-methylene phthalide, C₈H₄ { [1]C = CCl₂ phenone-carboxylic acid. Dichlor-methylene phthalide, C₈H₄ { [2]COO phthalide, C₈H₄ { [1]C = CH₂ phthalide, C₈H₄ { [1]C = CH₂ phthalide, C₈H₄ { [2]COO phthal

Isocoumarin, C_6H_4 $\left\{ \begin{bmatrix} 1 \end{bmatrix} CH = CH \\ \begin{bmatrix} 2 \end{bmatrix} CO - O \right\}$, melting at 47° and boiling at 285°, is formed in the distillation of silver isocoumarin-carboxylate. It readily volatilizes with steam. When digested with soda it becomes—

When digested with soda it becomes—

Anhydro-o-oxyvinyl Benzoic Acid, O(CH:CH[2]C₆H₄. CO₂H)₂, melting at 1839. When this body is heated with hydrochloric acid to 160° the anhydride, O(CH:CH[2]C₆H₄. CO)₂O, melting at 234°, results. The imide, O(CH:CH[2]C₆H₄CO)₂-NII, melting at 285°, is produced when alcoholic ammonia acts upon the anhydride at 170° (B. 27, 207).

Isocarbostyril, C_6H_4 $\left\{ \begin{bmatrix} I \end{bmatrix} CH = CH \\ [2]CO = NH \right\}$, melting at 208°, is isomeric with carbostyril (p. 277), the lactam corresponding to isocoumarin. It is formed when isocoumarin is heated to 130° with alcoholic ammonia, and upon heating isocarbostyril-carboxylic acid (p. 290) or its silver salt. It yields isoquinoline when distilled with zinc-dust (B. 27, 208).

3-Methyl-isocoumarin, C₆II₄ { [1]CH = C. CH₃, melting at 118°, is formed when { [2]CO - O }, melting at 118°, is formed when to 180° with hydrochloric acid. This latter body results from the action of sodium

to 180° with hydrochloric acid. This latter body results from the action of sodium acetate and acetic anhydride upon o-cyanbenzyl cyanide (B. 27, 831). Similarly o-cyanbenzyl cyanide furnishes an additional series of homologues of isocoumarin, all of which are characterized by their ready transposition into isocarbostyrils (see B. 29, 2543, etc.).

Ammonia converts 3-methyl-isocoumarin into the corresponding 3-Methylisocarbostyril, melting at 211° (B. 25, 3563).

Bergapten, $CH = CH \ C_0H(OCII_3)$ $CH = CH \ CO$ (?), melting at 188°, appears to be a derivative of oxyvinylcoumarin. It separates, on standing, from red bergamot oil, which is obtained by pressing out the fresh hulls of Citrus Bergamia Risso (B. 26, R. 234).

2. Phenylene Aldehydo-carboxylic Acids.—p-Aldehydo-cinnamic Acid, CHO-[4]C₆II₄. CH: CH: CO₂H, melting at 247°, is obtained from terephthal aldehyde by the Perkin reaction (p. 274) (A. 231, 375).

3. Phenylene Dicarboxylic Acids. —o Cinnamyl Carboxylic Acid, CO, H[2]C, H.

CH: CH. CO., H, melts at 174°, and reverts again to phthalidacetic acid. It is produced when phthalidacetic acid is digested with alkalies and by carefully oxidizing β -naphthol with potassium permanganate (B. 21, R. 654). More energetic oxidation produces carbophenyl glyoxylic acid (p. 265).

o-Cyan-cinnamic Acid, CN[2]C6H4CH: CH. CO2H, melting at 252°, is produced when sodium acetate and acetic anhydride act upon a-cyanbenzal chloride, and

also from o-amido-cinnamic acid (B. 24, 2574; 27, R. 262).
p-Cinnamyl Carboxylic Acid is obtained from terephthal-aldehydic acid and sodium acetate. It is an insoluble, infusible powder (A. 231, 369).
o-Phenylenediacrylic Acid, C₈H₄[1,2](CH:CH.CO₂H)₂, melts above 300°. It is produced when alcoholic potash acts upon o-xylylene dichlordimalonic ester (B. 19, 435). p-Phenylenediacrylic Acid is obtained from p-aldehydo-cinnamic ester with sodium

acetate and acetic anhydride (A. 231, 377), and from p-xylylene dibromdimalonic ester.

4. Phenylolefine Ketols.—Oxymethylene Acetophenone, C₆H₅. CO. CH: CH. OH, when separated from its sodium compound, is a very unstable oil. Its sodium derivative is formed when sodium ethylate acts upon formic ester and acetophenone. Formerly, oxymethylene acetophenone was considered to be benzoyl acetaldehyde (p. 250). Constitution of the oxymethylene compounds—see 1, 319. Phenylhydrazine converts it into diphenylpyrazole (see this); hydroxylamine unites with it to form benzoylacetaldoxime (p. 250).

5, 6. Phenyl-oxyolefine and Diolefine Carboxylic Acids.—Oxymethylene-phenyl-

acetic Ester, $C_6H_6C(CO, C_2H_6)$: CHOH—see formyl phenylacetic ester, p. 256. β -Ethoxycinnamic Ester, $C_6H_6C(OC_2H_6)$: CH . $CO_2C_2H_6$, boiling at 171-173°, is obtained from benzoyl acetic ester and orthoformic ester. The corresponding acid melts at 162° with evolution of carbon dioxide and the formation of β -phenylvinylethyl ether (p. 271) (B. 29, 1005).

Phenyl-a-oxy-crotonic Acid, C₆H₅CH: CH. CH(OH)COOH, melting at 137°, is prepared by saponifying its nitrile, cinnamyl-aldehyde cyanhydrin, melting at 80°, with cold concentrated hydrochloric acid. On boiling with hydrochloric acid the acid is

readily rearranged to benzoyl propionic acid (p. 261) (B. 29, 2582).

 β -Benzylangelic Lactone, C_6H_6 . CH_2C CH_3 , is obtained in the distillation of the contract of the c tion of benzyl-lævulinic acid (p. 261).

d-Oxycinnamylidene Acetic Acid.

Its lactone is *phenylcoumalin*, C₈H₈.C:CH.CH:CH.CO , melting at 68°, and found in coto-bark (B. 29, 2659; R. 1116).

7, 8. Phenyl-olefine- and diolefine-a-keto-carboxylic acids result from the condensation

of aromatic aldehydes with pyroracemic acid.

Cinnamyl Formic Acid, C₆H₅. CH: CH. CO. CO₂H, a bright yellow gummy mass, is obtained from its nitrile, cinnamyl cyanide, CaH5. CH: CH. CO. CN (B. 14, 2472), melting at 140°.

The ortho-nitro derivative is similarly formed from o-nitrobenzaldehyde and pyro-racemic acid. It melts at 135°, and is changed by alkalies, even in the cold, with elimi-

nation of oxalic acid, into indigo.

3,4-Methylene-dioxycinnamyl Formic Acid, (CH₂O₂)[3,4]C₆H₃. CH: CH. CO.CO.H, melting at 148-150°, and piperonylene-pyroracemic acid, (CH.O.)[3,4]-C.H.CH.CH.CH.CO.CO.H, melting at 165-167°, are formed from piperonal

and piperonyl acrolein (p. 272).

9. Phenyl-olefine-B keton Carboxylic Acids result from the condensation of acetoacetic ester and aromatic aldehydes with hydrochloric acid gas, or, better, primary or secondary amines in the cold (B. 29, 172). Benzal Acetoacetic Ester, C. H. CH: C<CO.C.H₅, melting at 59° and boiling at 181° (17 mm.) (A. 281, 63). The m-nitroester melts at 112° (B. 26, R. 448). Allyl Benzoyl Acetic Ester, C6H5.CO.-CH. < CO₂C₂H₆ CH: CH₂, melts at 122° (B. 16, 2132).

Benzal Diethyl Acetoacetic Ester, C_6H_6 . $CH:CH:COC(C_2H_6)_2$. $CO_5C_1H_9$ melts at 101°.

10. Phenyl-olefine-y-ketone Carboxylic Acids result by the condensation (1) of side-hydes and ketone-carboxylic acids with acids or alkalies; (2) of olefine dicarboxylic anhydrides—e.g., maleIc acid anhydride, citraconic anhydride, and benzenes with alaminium chloride.

β-Benzoyl Acrylic Acid, C₆H₅. CO. CH: CH. CO₂H, melts at 96° when sahydrous. It results from the action of sulphuric acid upon maleIc anhydride (see abore), as well as from phenyl-γ-keto-α-oxybutyric acid (p. 261). Trichlorethidene Acetophenone, C₆H₅. CO. CH: CH. CCl₃, melting at 102°, is produced when sulphuric acid acts u; on chloral-acetophenone (p. 261). β-Benzoyl Crotonic Acid, C₆H₅. CO. C(CH₃): CH. CO₂H, melting at 113°, is obtained from citraconic anhydride (B. 15, 891).

 β -Benzal-lævulinic Acid, C_8H_5 . CH: $C<\frac{CO}{CH_2}$. CO_2H_7 , melting at 125°, is produced by the condensation of benzaldehyde and lævulinic acid in acid solution. It parts with water upon distillation and forms 3-aceto-1-naphthol. Phenylitaconic acid is formed by its oxidation, and β -benzyl-lævulinic acid by its reduction. Hydroxylamine products the neutral lactoxime, Benzal-lævoxime, C_8H_5 . CH: $C<\frac{CH_3CO}{CH_3}$. When benzaldehyde and lævulinic acid acid by C:N. O, melting at 94°.

When benzaldehyde and levulinic acid condense in alkaline solution the product is d-Benzal-levulinic Acid, C₆H₆CH: CH. CO. C₂H₄. CO₂H, melting at 120°. It

yields bensal-angelic lactone, melting at 90° (B. 24, 3202), upon distillation.

11, 12. Phenylolefine- and diolefine Dicarboxylic Acids.—Benzal Malonic Acid, C₆H₅. CH: C(CO₂H)₂, melts with production of cinnamic acid and allocinnamic acid (p. 274). It is formed in the condensation of benzaldehyde, malonic acid, and glacial acetic acid. Its ethyl ester, boiling at 198° (13 mm.), is obtained from benzaldehyde, malonic ester, and hydrochloric acid. It adds to itself more readily than the free acid. Andline as well as phenylhydrazine converts the methyl ester into β-Anilido- and β-Phenylhydrazido-benzyl-malonic Methyl Ester, melting at 117° and 94° (B 29, 813). When substituted benzaldehydes are used, substituted benzal-malonic acids result —e.g., nitrobenzal malonic acid, which is reduced by ferrous sulphate and ammonia to β-carbostyril carlovylic acid B, 27, R, 25.2)

to β-carbostyril carboxylic acid (B. 21, R. 253).

a-Cyan-cinnamic Acid, Half-nitrile of Benzal Malonic Acid,

 $C_6 II_5$. CII: $C<\frac{CO_2 H}{CN^2}$, melting at 180°, is obtained by the action of cyan-acetic acid in the heat upon benzaldehyde, or when it is boiled with cyanacetyl chloride. When heated it passes into the nitrile of cinnamic acid (p. 274). The methyl and ethyl ester melt at 70° and 50°. A large number of half-nitriles of unsaturated, aromatic malonic acids of related constitution have been obtained by the union of readily accessible, aromatic aldehydes with cyan acetic acid (B. 27, R. 262). Nitrile Acid Amide, dinitrile, and diamide of benzal malonic acid, melting at 123°, 87°, and 190°, have also been synthesized by the condensation of benzaldehyde with cyanacetamide, malonitrile, and malonamide (B. 28, 2251).

 β -Carbostyril Carboxylic Acid, C_8II_4 $\left\{ \begin{array}{l} [1]CII:C:CO_2H\\ [2]NH:CO \end{array} \right\}$, is formed from 0-amidobenzaldehyde upon heating it with malonic acid to 120°, and also from 0-nitrobenzal malonic acid (B. 21, R. 353). Its silver salt, when heated, yields carbostyril.

malonic acid (B. 21, R. 353). Its silver salt, when heated, yields carbostyril.

Coumarin Carboxylic Acid, C_6H_4 [1]CH: C. CO₂H, melting at 187°, breaks down at 290° into carbon dioxide and coumarin (p. 281). It is obtained from salicylaldehyde, malonic acid, and glacial acetic acid, as well as from—

Cyan-coumarin, C_6H_4 $\left\{ \begin{bmatrix} 1 \end{bmatrix} CH : C. CN \\ 2 \end{bmatrix} CO \right\}$, melting at 182°. This latter body may be prepared by the action of dilute sulphuric acid upon o-oxybenzaldicyanacetic ester, $HO[2]C_6H_4CH[CH(CN)CO_2C_2H_5]_2 + \frac{1}{2}H_2O$, melting at 140°. This is a condensation product of salicylaldehyde and cyanacetic ester (B. 27, R. 576).

Cinnamenyl Malonic Acid, Phenyl-butine Dicarboxylic Acid, CaH5. CH: CH. -

Chinamenty Malonic Acid, Prenyi-onine Dicarooxytic Acid, C₆H₅. Ch: Ch: CCO₂H)₂, melts at 208° (B. 19, R. 350). Cinnamenyl Cyanacrylic Acid, C₆H₅. Ch: Ch. Ch: C(CN)CO₂H, melts at 212°.

Piperonylene Malonic Acid, (CH₂O₂)[3,4]C₆H₅. Ch: Ch. Ch: C(CO₂H)₂, melts at 205° with decomposition into CO₂ and piperic acid (p. 285) (B. 28, 1190). Phenyl Allyl Malonic Acid, C₆H₅C(CH₂. Ch: Ch₂)(COOH)₂, melts with decomposition at 145°. Its ester is formed when allyl iodide acts upon phenyl-malonic ester (B. 29, 2600).

CH . CO₂H , changes below 100° into its anhydride, C₆H₅ . C . CO₂H Phenyl Maleic Acid,

melting at 119°, which is produced when bromine and PBr, act upon phenylsuccinic acid, and the reaction product is treated with water. Phenylmalic acid is formed simultaneously (B. 23, R. 573).

Phenyl Itaconic Acid, CaH5. CH: C. CO3H CH₂. CO₃H, melting at 172°, is formed (1)

from succinic ester, benzaldehyde, and sodium ethylate; (2) from phenyl paraconic ester and sodium ethylate. When fused, particularly under reduced pressure, it separates into water and its anhydride, melting at 163-166°, which in every fusion changes in a slight degree to isomeric *phenylcitraconic anhydride*, melting at 60°. Water changes the latter to *phenylcitraconic acid*, melting at 103-106°. If phenylcitraconic acid in chloroform solution, to which a little bromine is added, be exposed to sunlight, it becomes phenylmesaconic acid, melting at 210°.

The conversion of phenylitaconic acid in chloroform solution, to which a few drops of a dilute bromine solution have been added, into phenylaticonic acid, melting at 148° (B. 26, 40, 2082; 27, 2405) (I, 465), when exposed to sunlight, is certainly very remarkable.

Coumarin-propionic Acid, C₆H₄ { [1]CH = C. CH(CH₃)CO₂H, melting at 171°,

is formed, together with o-oxyphenyl methylisocrotonic acid, from salicylaldehyde, sodium pyroracemate, and acetic anhydride. It passes into a-ethyl coumarin when it is distilled (A. 255, 285).

Methyl Phenyl Itaconic Acid, $C_8H_5C(CH_3) = C(CO_2H)CH_2$. CO_2H , melts with decomposition at 161-163°. It is obtained from succinic ethyl ester, acetophenone, and

sodium ethylate in ether (A. 282, 288).

Phenyl Glutaconic Acid, C₆H₅. C(CH₂. COOH): CH. COOH, melting at 154°, has been obtained from the condensation product formed in the union of phenylpropiolic

ester with sodium malonic ester (B. 27, R. 163).

Benzal Glutaric Acid, C₄H₅. CH: C(CO₂H)CH₂. CH₃. COOH (A. 282, 338).

Benzyl Glutaconic Ester, C₈H₅. CH₂. CH(COOH)CH: CH. COOH, melts at 145° (A. 222, 261). Its ethyl ester, boiling at 203° (10 mm.), when treated with ammonia at 100°, forms dihydroxybenzyl pyridine, melting at 184° (B. 26, R. 318). (Compare constitution of pyridine.)

13. Phenylene Oxyolefine Dicarboxylic Acids.—Phthalyl acetic acid and isocoumarin carboxylic acid have the same relation to each other that methylene phthalide sustains to isocoumarin. Phthalyl acetic acid and its homologues have been obtained by applying the Perkin reaction to phthalic anhydride:

Phthalyl Acetic Acid, C_8H_5 $\begin{cases} C = CH \cdot CO_9H \\ COO \end{cases}$, melts with decomposition above

260°. When distilled under greatly diminished pressure it breaks down into carbon dioxide and methylene phthalide (p. 285). Salts of benzoylaceto-carboxylic acid (p. 263) are obtained by dissolving it in alkalies. When it is heated with water to 200° it breaks down into carbon dioxide and o-acetylbenzoic acid. When heated with ammonia it forms *Phthalimide Acetic Acid*. The alkylamines react analogously.

Sodium ethylate converts phthalylacetic acid into the sodium salt of diketohydrindene

carboxylic acid (see this) (B. 26, 953).

200

Isocoumarin Carboxylic Acid, C_8H_4 $\left\{ \begin{bmatrix} 1 \end{bmatrix} CH = C - CO_2H \\ [2]CO - O \end{bmatrix}$, melting at 237°, is formed when o-carbophenyl glyceric acid lactone (p. 265) is heated to 160° with hydrochloric acid. See isocoumarin. Ammonia converts it quite readily into isocarbostyril carboxylic acid, C_8H_4 $\left\{ \begin{bmatrix} 1 \end{bmatrix} CH = C \cdot CO_2H \\ E^2CO - NH \right\}$, melting at 320° (B. 25, 1138). Boiling caustic potash decomposes it into o-toluic acid and oxalic acid (B. 28, R. 770).
14. Phenylene Oxyolefine Tricarboxylic Acids. — Phthalyl Malonic Ester, $\begin{bmatrix} 1 \end{bmatrix} C = C(CO_2C_1H_8)_3 \\ (1 \end{bmatrix} C = C(CO_2C_2H_8)_3 \\ (1 \end{bmatrix} C = C(CO_2C_2H_8)_3 \\ (2 \end{bmatrix} COO$ ester (p. 265), from phthalyl chloride and sodium malonic ester (A. 242, 46). Phthalyl Cyanacetic Ester, C_8H_4 $\begin{bmatrix} 1 \end{bmatrix} C = C < CO_2C_2H_8 \\ (2 \end{bmatrix} COO$, melting at 175°, is made from phthalyl chloride and sodium cyanacetic ester (B. 26, R. 370).

B. HYDROAROMATIC SUBSTANCES WITH SINGLE-NUCLEUS, HYDROBENZENE DERIVATIVES.

It was shown in the introduction to the carbocyclic compounds that the treatment of the hydroaromatic derivatives presupposed a knowledge of the aromatic bodies (p. 18). Indeed, numerous reactions which led to the hydroaromatic compounds, especially the additions, were described in connection with the aromatic substances. Many bodies discussed under the aromatic derivatives—e. g., the quinones—are rather to be viewed as derived from the hydroaromatic hydrocarbons. And reactions were also learned in the discussion of the fatty bodies which will again be encountered, and through which mono-nucleus, hydroaromatic substances are produced. The terpenes and camphor will be included in the hydroaromatic derivatives.

I. HYDROAROMATIC HYDROCARBONS.

Hexahydrobenzene is the parent hydrocarbon of the hydroaromatic substances. Tetra- and di-hydrobenzene bear the same relation to it that an olefine and a diolefine show to the paraffin, having the same number of carbon atoms.

The hexahydrobenzenes, which are isomerides of olefines with a like number of carbon atoms, resemble the paraffins in chemical deportment; they belong to the cycloparaffins (compare 1, 89; 11, 17), while the tetrahydrobenzenes belong to the cyclo-olefines, the dihydrobenzenes to the cyclodiolefines, and benzene is the simplest imaginable cyclotriolefine, if we accept the formula proposed for it by Aug. Kekulé.

Berthelot (1867) first effected the reduction of benzene to hexahydrobenzene. It was obtained pure by Baeyer (1894) in the course of an investigation in which he demonstrated how the simplest representatives of the hydroaromatic bodies—hexahydrobenzene, tetrahydrobenzene, and dihydrobenzene—could be prepared from p-diketohexamethyl-

ene, a decomposition product of succino succinic ester (p. 305). Before beginning a detailed description of the hydroaromatic hydrocarbons it may be well to briefly present the steps of this research in a diagram. The inclosed numbers following the names refer to the formulas of the diagram.

p-Diketohexamethylene (1) yields quinite (2) by reduction, which hydrogen bromide changes to p-dibromhexamethylene, and hydrogen iodide into the monoiodhydrin (4) of quinite, along with p-diiodhexamethylene. Quinite monoiodhydrin, when reduced, yields oxyhexamethylene (5). Hydrogen bromide and iodide convert oxyhexamethylene (6) into brom- and iod-hexamethylene (6, 7). When p-dibromhexamethylene and monobromhexamethylene are heated with quinoline the latter yields tetrahydrobensene (8), and the former dihydrobensene (9); whereas mono-iod-hexamethylene is reduced by zinc-dust and glacial acetic acid to hexahydrobensene (10):

Compare the tetrahydrobenzenes (p. 293) for additional methods for the preparation of hydrobenzene derivatives.

The following values (V) and differences (D) were observed by Stohmann in determining the heats of combustion and the boiling points of benzene, the three hydrobenzenes, and hexane:

The differences calculated from these numbers would have to be equal if the changes were of like character. The magnitude of these differences expresses, therefore, the magnitude of the changes involved in the reduction (A. 278, 115). Consult Brühl, B. 27, 1065, upon the value of molecular refraction in the determination of structural differences.

1 a. HEXAHYDROBENZENES, NAPHTHENES [CYCLOHEXANES].

Hydroaromatic hydrocarbons constitute the chief portion of Caucasian petroleum (1, 88) (Beilstein and Kurbatow, B. 13, 1818). Markownikow has, therefore, designated them naphthenes. Hexahydrobenzenes have also been discovered in the tar from bituminous coal and in that from certain shales, as well as in the resin-oils obtained from the distillation of colophonium. They have been made artificially by reducing aromatic hydrocarbons with hydriodic acid at high temperatures. Hexahydrobenzene resists decomposition by means of hydrogen very strongly

(A. 278, 88). The hexahydrobenzenes are more easily obtained by reducing their halogen substitution products.

When hydriodic acid is used as a reducing agent, under certain circumstances alkylpentamethylenes appear to form by a process of isomerization; these are isomeric with the hexamethylenes. Thus, methylpentamethylene is formed together with hexamethylene (B. 30, 1214).

The hexahydrobenzenes are distinguished from the olefines isomeric with them by their higher specific gravity and their inability to take up bromine. Like the paraffins, they are first changed by chlorine into mono-chlor substitution products, from which esters of monacid alcohols, amines, and tetrahydrobenzenes can be prepared by wellknown methods. Substituted aromatic hydrocarbons are obtained from the hexahydrobenzenes by the action of bromine and aluminium bromide, as well as by the action (although with difficulty) of nitric acid and sulphuric acid. However, nitrohydrobenzenes have been obtained by the use of dilute nitric acid (B. 25, R. 107; 28, 577).

```
Hexahydrobenzene . . . boils at 79°; sp. gr. 0.7473 (0°)
Hexahydrotoluene . . . " "100°; " "0.7778 (0°)
Hexahydro-m-xylene . . "118°; " "0.7814 (0°)
Hexahydrocumene . . "148°; " "0.7870 (20°)
Hexahydromesitylene . "137°; " "0.7812 (12°)

1,3,4-Hexahydropseydocumene "17820000 "0.7812 (12°)
               Hexahydrocymene, see Terpenes, p. 307, and B. 29, 317.
```

Hexahydrobenzene (B. 28, 1234), hexahydrotoluene, hexahydro-m-xylene, and hexahydropseudocumene have been found in the naphtha of Caucasian petroleum, while hexahydrotoluene, hexahydro-m-xylene, hexahydrocumene, and hexahydrocymene are present in resin-oil.

Hexahydrobenzene, Naphthene, Hexamethylene, Ring-hexene, Cyclohexane, CH₂ CH₃ CH₃ CH₂ CH₂, results from the reduction of iodhexamethylene (p. 291, and B. 28, 1022; 30, 391), and by the action of sodium upon synthetic hexamethylene bro-It is a liquid with an odor like that of petroleum (A. 278, 110; B. 27, 216).

Hexahydrotoluene, Heptanaphthene, Methylcyclohexane, has also been made from suberyl alcohol (p. 28) by the action of HI at 140° (B. 25, R. 858), and from perselle (see 1), as well as from synthetic methyl hexamethylene ketone by means of the corresponding alcohol (B. 29, 731). Bromine and aluminium bromide convert it into pentabromtoluene, melting at 282°.

Hexahydro-m-xylene, Octonaphthene, [1,3-Dimethylcyclohexane], is obtained from camphoric acid, from heptanaphthene carboxylic acid by means of HI (A. 225, 110; B. 24, 2718; 25, 920), and from hexahydro-2,6-dimethyl phenol (p. 294).

Hexahydro-p-xylene is obtained from brom-camphor by means of ZnCl, at 160°

(B. 13, 1407).

Hexahydropseudocumene, Nonaphthene, 1,3,4-Trimethylhexamethylene, from hexahydrotrimethyl phenol (B. 29, 215), when acted upon with bromine and aluminium bromide, yields tribrompseudocumene. 1,3-Methylisopropylcyclohexane, symmenthane, boiling at 167°, is formed by the reduction of its iodine substitution product.

[1,3]-Diethylhexahydrobenzene, boiling at 170°, sp. gr. 0.7957 (22°/4°), n_D = 1.4388 (20°), is isomeric with hexahydrocymene. It is obtained from hexahydro-2,6-

diethyl phenol (p. 294).

Halogen Substitution Products of the Hexahydrobenzenes.—Formation: (1) From the hexahydrobenzenes by the introduction of chlorine. (2) By the addition of halogens and halogen hydrides to di- and tetrahydrobenzenes. (3) By the addition of halogens to benzenes and halogen benzenes (p. 57). (4) From the oxyhexahydrobenzenes through the exchange of hydroxyl groups for halogens.

The third method has brought to light peculiar isomeric phenomena. Two isomeric benzene hexachlorides, two isomeric chlorbenzene hexachlorides and benzene hexachlorides have been found. The disposition on the part of chemists is to ascribe the Two isomeric cause of this isomerism to the different positions of the attached chlorine atoms with reference to the plane of the carbon ring, as in the case of the isomeric trithioaldehydes (1, 203), and the isomeric tri-, tetra-, and pentamethylene dicarboxylic acids (pp. 23, 24, 27). At the conclusion of the hexahydrobenzenes only those addition products obtained according to method 3 will be discussed, which eventually, by loss of halogen hydride,

pass into benzene halogen substitution products.

a- or trans-Benzene Hexachloride, $C_8H_8Cl_8$, melting at 157° and boiling at 218° (345 mm.), decomposes into 3HCl and unsym. trichlorbenzene (p. 58). β - or cis-Benzene Hexachloride melts and sublimes near 310°. a-Benzene hexachloride was made by the action of chlorine upon benzene in sunlight (1825, Faraday; 1835, Mitscherlich, Pogg. A. 35, 370). a- and β -Benzene hexachlorides are produced when chlorine is conducted into boiling benzene (1884, Meunier; B. 18, R. 149; 19, R. 348), or, better, into a mixture of benzene and 1 per cent. sodium hydroxide. The a-body is separated by distillation in steam from the less volatile β -derivative (B. 24, R. 632), or by means of chloroform from the more sparingly soluble β -compound. The latter is the more resistant of the two modifications. When heated with alcoholic potash it is converted with greater difficulty than the a-body into unsym. trichlorbenzene. It is not affected by alcoholic potassium cyanide, but when boiled with this reagent the a-variety is converted into unsym. trichlorbenzene. Zinc in alcoholic solution changes the a-modification into benzene (Z. f. Ch., 1871, N. F. 7, 284, 293).

a- and β-Chlorbenzene Hexachloride, C₈H₅Cl₇, melting at 146° and 260°, yield 1,2,3,5-tetrachlorbenzene with alcoholic potash (A. 141, 101; B. 25, 373). 1,2,4-

Trichlorbenzene Hexachloride, C₆H₃Cl₉, melts at 95°.

a Benzene Hexabromide, C₆H₆Br₆, melting at 212°, results from the action of broming upon benzene in multiple at 212°, results from the action of broming upon benzene in multiple at 212°, results from the action of broming upon benzene in multiple at 212°, results from the action of broming upon benzene in multiple at 212°, results from the action of broming upon benzene in multiple at 212°, results from the action of broming upon benzene in multiple at 212°, results from the action of broming upon benzene in multiple at 212°, results from the action of broming upon benzene in multiple at 212°, results from the action of broming upon benzene in multiple at 212°, results from the action of broming upon benzene in multiple at 212°, results from the action of broming upon benzene in multiple at 212°, results from the action of broming upon benzene in multiple at 212°, results from the action of broming upon benzene in multiple at 212°, results from the action of broming upon benzene in multiple at 212°, results from the action of bromine upon benzene in sunlight, and when bromine acts upon boiling benzene. When it splits off IIBr, 1,2,4-tribrombenzene is formed (Pogg. A. 35, 374). It is isomorphic with a benzene hexachloride (B. 18, R. 553). When bromine acts upon benzene in the presence of dilute caustic soda, a second compound $-\beta$ -Benzene Hexabromide, melting at 253° (B. 29, R. 1138)—is formed together with the first body.

I b. TETRAHYDROBENZENES, NAPHTHYLENES [CYCLOHEXENES].

Tetrahydrotoluene has been discussed together with hexahydrotoluenes and allied hydrocarbons found in the essence of resin. The hexahydrobenzenes yield tetrahydrobenzenes by the introduction of chlorine and the exit of HCl. The hydrocarbons—e. g., Carvomenthene and Menthene (see these)—obtained from terpenes and their derivatives belong to the tetrahydrobenzenes.

Tetrahydrobenzene, CH₂—CH₂—CH₃—CH₄ boiling at 82-84° (p. 291), is pro-

duced on distilling monobromhexamethylene (p. 294) with quinoline. It is a colorless liquid, resembling petroleum. It has less of the leek odor than dihydrobenzene. It is colored yellow by concentrated sulphuric acid. The dibromide is a liquid. The nitrosochloride melts at 152°. The nitrosate, NO. C₈H₁₀. O. NO₂, melts at 150° with decomposition (A. 278, 107). Tetrahydrotoluene is obtained from pulegone (A. 289, 343).

Different homologous tetrahydrobenzenes have been obtained from hexahydrophenols (p. 294) by the removal of water with P₂O₅. Methyl-, dimethyl-, Methyl-iso-propyl-tetrahydrobenzenes boil at 105°, 124°, and 109° (communicated by E. Knöve-

nagel).

1 c. DIHYDROBENZENES [CYCLOHEXADIËNES].

Very probably some of the naturally occurring terpenes belong to the dihydrobenzenes. The artificially prepared representatives of the dihydrobenzenes are very similar in deportment to them. The method of preparing the simplest of the hydrocarbons in this class—dihydrobenzene -from succino-succinic ester has already been discussed (p. 291). Mono-alkyl and di-p-alkyl-dihydrobenzenes were made in like manner: from mono- and di-alkylsuccinosuccinic esters (B. 26, 232).

A second method for the preparation of dihydrobenzenes is based upon the rearrangement of the dihydroresorcinol derivatives obtained in the condensation of δ -ketonic esters (p. 297). The dihydroresorcinols yield dihydric alcohols upon reduction; these, by the exit of two molecules of water, become dihydrobenzenes. Thus far only one phenyl-dihydrobenzene has been prepared in this manner (A. 289, 137).

boiling at 84-86°, results when p-dibromhexamethylene is heated with quinoline (p. 291). It is a leek-like liquid, resembling benzene. It resinifies, like the terpenes (p. 291), on exposure to the air. It decolorizes a solution of KMnO, instantaneously, and takes on a blue color when treated with concentrated sulphuric acid (see sylvestrene, p. 308). Its tetrabromide melts at 185° (B. 25, 1840).

Dihydrotoluene, C₇H₁₀, boiling at 105-108°, is obtained from toluene by the action

of PH,I (A. 155, 271).

Dihydro-o-xylene, Cantharene, boiling at 135°, is produced when cantharic acid, C₁₀II₁₂O₄, a rearrangement product of cantharadine, is distilled with caustic lime. Its odor is like that of a terpene, and it resinifies on exposure to the air (Piccard, 1878; B. 25, 2453).

Dihydro-m-xylene, boiling at 133°, sp. gr. 0.8275 (20°), is obtained when methyl heptenone, (CII₃)₂CH. CII = CH. CH₂COCH₃, is condensed with ZnCl₂ (A. 258,

326).

Dihydro-p-xylene boils at 134°. Dihydro-p-diethyl Benzene boils at 180-185°. Dihydro-p-methylisopropyl Benzene, Dihydro-p-cymene, boils at 174°.

2. RING-ALCOHOLS OF THE HYDROAROMATIC HYDRO-CARBONS.

In this group are included quercite and inosite, formerly classed with the sugars, as well as the ring alcohols of the terpane or menthane group among the terpenes (p. 313), while other members have been obtained by the reduction of aromatic or hydroaromatic compounds, but chiefly from the corresponding ketones.

Hexahydrophenol, [Cyclohexanol], $C_6H_{11}(OH)$, melting at $+15^\circ$ and boiling at 158° (720 mm.), is formed by the action of zinc-dust and glacial acetic acid upon p-iodhexahydrophenol, the reaction product obtained from quinite and hydriodic acid. Its odor is like that of fusel oil. It is more readily soluble in water than the aliphatic alcohols containing six C-atoms (B. 26, 229). Its acetyl derivative melts at 104° . Hydrobromic acid converts it into bromcyclohexane, boiling at 162° (720 mm.). See tetrahydrobenzene.

Hexahydro-2,6-dimethyl Phenol, boiling at 174°, and Hexahydro-2,6-diethyl Phenol, melting at 77° and boiling at 210°, along with a series of additional homologues, have been prepared by the reduction of the corresponding ketones (p. 296).

Hexahydrophenols have also been obtained from the synthetic keto-R-hexenes (p. 298). This has been accomplished by treating the latter with sodium and alcohol. The hexahydrophenols appear to occur in two probably stereoisomeric forms. A chromic acid mixture oxidizes them to keto-R-hexanes. Their hydriodic esters are reduced by zinc-dust and glacial acetic ester to cyclohexanes, and when they lose water through the action of P₂O₅, cyclohexenes result (privately communicated by E. Knövenagel).

Quinite, [Cyclohexane-1,4-diol], HOCH $< \frac{CH_1}{CH_1} = \frac{CH_2}{CH_2} > CHOH$, melting at 144°, is formed from p-diketohexamethylene (p. 296) when treated with sodium amalgam in the presence of carbon dioxide. This was demonstrated by A. v. Baeyer in 1892. It tastes sweet at first, then bitter, and is readily soluble in water and in alcohol. Chromic

acid oxidizes it to quinone (B. 25, 1038). Quinite serves for the preparation of the simple hydride derivatives of benzene (B. 26, 229). Hydriodic acid converts it into p-iodcyclohexanol and p-di-iodcyclohexane. By reduction the first yields hexahydrophenol, the second cyclohexane (p. 293). p-Dibromcyclohexane passes readily into dihydrobensene (p. 294) (B. 26, 230). 2,5-Dimethyl Quinite is formed from the corresponding diketone (B. 25, 2122).

Phloroglucite, s-Trioxyhexamethylene, [Cyclohexane-1,3,5-triol],

HOCH $\langle \text{CH}_3 - \text{CH}(\text{OH}) \rangle \rangle \text{CH}_3 + 2\text{H}_3\text{O}$, melts when anhydrous at 184°. It is formed when phloroglucin is reduced in an approximately neutral solution with sodium amalgam (B. 27, 357).

Quercite, [Cyclohexanpentol], CH₁ < CH(OH) — CH(OH) > CH(OH), melting at 235°, [a]_D = +24.16°, occurs in acorns. The aqueous extract of the latter can be freed of glucoses by fermentation with beer-yeast. Quercite does not ferment with Hydriodic acid converts it into benzene, hexane, phenol, quinone, and hydroquinone (Prunier). Nitric acid oxidizes it to mucic acid and trioxyglutaric acid (see vol. 1). A solution of potassium permanganate converts it chiefly into malonic acid, although oxalic acid and carbonic acid are formed simultaneously (B. 29, 1762).

Inosite, Hexahydrohexaoxybenzene, [Cyclohexanhexene], CeHe(OH)e, is known in

one optically inactive and two optically active modifications.

i-Inosite, *Phaseomannite*, *Dambose*, $C_0H_0(OH)_0 + 2H_0O$, melts at 225° when anhydrous. It occurs in the muscles of the heart and in the urine when there has been an excessive consumption of water; also in unripe beans (Phaseolus vulgaris) and peas. If heated to 170° with hydriodic acid, it yields phenol, di-iodphenol, and traces of benzene (Maquenne). Concentrated nitric acid oxidizes it to di- and tetra-oxyquinones (p. 170), and to rhodizonic acid (p. 171) (B. 20, R. 478; 23, R. 26).

Dambonite, C₆H₆(OH)₄(OCH₃)₂ + 3H₂O, is the dimethyl ether of i-inosite. It occurs in the caoutchouc from Gabon.

i-Inosite Hexaacetate melts at 211°.

d-Inosite, melting at 247°, $[a]_D = +65^\circ$, from pinite by the action of hydriodic acid, behaves like i-inosite with nitric acid. Pinite, *Materite*, $C_aH_a(OH)_b(OCH_a)$, melting at 186°, $[a]_D = +65.51^\circ$, is present in the juice of *Pinus lambertina*, also in the caoutchouc from Mateza roritina of Madagascar.

1-Inosite, melting at 238°, [a]_D = -55°, from quebrachite by means of hydriodic acid, behaves toward nitric acid just like i-inosite. Quebrachite, C₆H₆(OH)₅OCH₅,

melting at 186°, $[a]_D = -80^\circ$, occurs in the quebracho-bark.

Phenose, C₆H₆(OH₆) (?), is an amorphous, readily soluble substance, deliquescing in the air. It has a sweet taste and reduces Fehling's solution, but is not capable of fermentation. It has been obtained by the action of a soda solution (A. 136, 323) upon the addition product of benzene with three molecules of hypochlorous acid, $C_6H_6\begin{Bmatrix} Cl_2\\ (OH)_3 \end{Bmatrix}$.

Ring-alcohols of Tetrahydrobenzene: Tetrahydrophenol, [Δ_3 -Cyclohexenol],* CHOH, boiling at 163°, is formed when p-iodcyclohexanol (p. CH, — CH. 291) is distilled with quinoline.

3. RING-AMINES OF THE HYDROAROMATIC HYDROCARBONS

have been obtained by the reduction of the corresponding oximes with sodium in alcoholic solution. The ring-amines of the terpane and menthane groups, discussed under the terpenes, belong in this class. Amidohexamethylene, C₆H₁₁NH₂, is isomeric with the methyl piperidines. It boils at 133°, smells like coniine, and dissolves sparingly in

 $[\]Delta$ indicates a double union; the added number (in this case β) that this carbon atom 3 is doubly linked to the carbon atom 4.

water. Its acet-derivative melts at 104°. The bensoyl compound melts at 147°. The phenylurea derivative melts at 180°. The phenylthiourea body melts at 147°.

o-Diamidohexamethylene, C₄H₁₀ [1,2](NH₂)₃, is an oil, boiling at 183-185°. It results when the amide of hexahydroanthranilic acid (p. 300) is treated with sodium hypobromite and then with hydrochloric acid. Like the aromatic o-diamines, it unites with benzaldehydes, forming aldehydines (p. 95) (A. 295, 187). m-Diamidohexamethylene, boiling at 193°, smells like ethylenediamine. It is

soluble in water. Nitrous acid decomposes it into nitrogen and dihydrobenzene (A. 228,

39). The diacet-compound melts at 256°.

p-Diamidohexamethylene, $C_8H_{10}[1,4](NH_2)_2$, is a liquid (B. 27, 1449).

4. RING-KETONES OF THE HYDROAROMATIC HYDROCARBONS.

(a) Ring-ketones of Hexahydrobenzenes.—Pimelin Ketone, [Cyclohexanon], Ketohexamethylene, CH₃ < CH₂ - CH₃ > CO, boiling at 155°, is an oil with an odor like peppermint. It results (1) by the oxidation of hexahydrophenol (p. 294); (2) in the reduction of phenol with alternating currents; (3) in the distillation of calcium n-pimelinate (1, 455). Upon reduction it yields [cyclohexanol] (p. 294), while nitric acid oxidizes it to adipic acid (1, 455). Its oxime melts at 88°. Its phenylhydrazone, melting at 74-77°, when acted upon by mineral acids loses ammonia and passes into tetrahydrocarbazole (see this) (A. 278, 100).

A series of alkylic keto-hexamethylenes has been obtained from the alkylic pimelic

acids:

2-, 3-, 4-Methylketohexamethylenes boil at 166°, 164°, and 163-165°; 2,6-Dimethyl- and 2,6-Diethylketohexamethylenes boil at 163° and 206°; 2,4.5-Trimethylketohexamethylene boils at 191° (B. 28, 1341, 2944; 29, 731; A. 295, 186). 3-Methylketohexamethylene has also been prepared in other ways. It results from the oxidation of 3-methylketohexahydrophenol with a chromic acid mixture; the latter body is produced in the reduction of synthetic 3-methylcycloketohexene (p. 298). It also appears in an optically active, dextro-gyrating modification by the decomposition of pulegon (see this), and, finally, in the decomposition of isopulegon (see this) (B. 30, 23). A 3.5,5 Trimethylketohexamethylene, boiling at 189°, is Dihydroacetophorone. It is formed when chromic acid oxidizes dihydroisoacetophorol, a reduction product derived from isoacetophorone.

Similarly, 3,5-Methylisopropylketohexamethylene, sym. Menthone, boiling at

222°, is obtained by the oxidation of the corresponding alcohol.

Diketohexamethylenes, Cyclohexandiones.

Theory predicts three isomeric diketohexamethylenes, two of which —dihydroresorcinol and tetrahydroquinone—are known. Dihydroresorcinol possesses the character of a feeble base, and is therefore to be viewed probably as a ring-shaped, unsaturated ketone alcohol.

Dihydroresorcinol, 1,3-Cyclohexandion, m-Diketohexamethylene,

CH₂ CO CH₃ or CH₂ CH₃ CO CH, melts with decomposition at 104-106°. It is produced upon introducing pure sodium amalgam into a boiling aqueous resorcinol solution while carbon dioxide is being conducted into it. It may be synthesized by the condensation of γ -acetylbutyric ester with sodium ethylate (p. 44). Dihydroresorcinol dissolves readily in water, alcohol, and chloroform, but with difficulty in ether. When heated to 150-160° with baryta-water it is decomposed so as to form y-acetylbutyric acid, and when oxidized it yields glutaric acid and carbon dioxide (A. 204, 260). It reacts acid and decomposes the alkali and alkaline earth carbonates. It also forms a dioxime, C₈H₈(NOH)₂ + 2H₂O. This melts at 154-157° when it is anhydrous; when reduced it becomes m-diamidohexamethylene. m-Dioxyhexahydroisophthalo-nitrile (p.

304) (A. 278, 20) is formed by adding prussic acid to dihydroresorcinol.

Homologues of dihydroresorcinol are similarly formed in the condensation of like d-ketone-carboxylic esters, as, for example, in the addition of malonic esters to alkylideneacetoacetic ester. When the latter is condensed with malonic ester through the agency of sodium ethylate, and the product then saponified, carbon dioxide is eliminated and there results methyldihydroresorcinol, melting at 126° (A. 289, 137; 294, 253):

Phenyldihydroresorcinol melts at 184° with decomposition. Dimethyldihydroresorcinol, (CH₃)₂C: [CH₃. CO]₂: CH₂, melts at 150°.

The homologous dihydroresorcinols react like simple dihydroresorcinol, both as dike-

tones and as unsaturated oxyketones.

Tetrahydroquinone, [1,4-Cyclohexandion], p-Diketohexamethylene, CO CH₃ - CH₃ > CO, melting at 78°, results upon saponifying succino-succinic ester with concentrated sulphuric acid, when it loses carbon dioxide (Baeyer, see p. 291), or when the same body is boiled with aqueous-alcoholic hydrochloric acid (private communication from R. Stollé). It unites with sodium bisulphite to a dioxime, melting at 192°; compare p-diamidohexamethylene. It forms quinite (p. 294) upon reduction;

see also a-dioxyhexahydroterephthalic acid (p. 304).
p-Dimethyl-p-diketohexamethylene, [2,5-Dimethyl-1,4-cyclohexandion], melting

at 93°, is obtained from p-dimethylsuccino-succinic ester (B. 25, 2122).

[Cyclohexantriones.] Phloroglucin yields derivatives which can be deduced from the formula of 1,3.5-trioxybenzene, and others which can be obtained from the formula of 1,3,5-triketohexamethylene. It was discussed at the conclusion of pyrogallol and oxyhydroquinone (pp. 164, 165), as were the hexa-alkyl derivatives of phloroglucin.

Triquinoyl, C₈O₈ + 8H₈O (p. 171), described with the quinones, is probably hexa-

ketohexamethylene.

Halogen Substitution Products of the Ring-ketones of Hexahydrobenzene.—These are formed in the continuous action of chlorine and bromine upon phenols, quinones and oxyquinones. Several of the keto chlorides can be readily rearranged into halogen ketopentene derivatives, and be decomposed into highly chlorinated fatty bodies: ketones, ketonic acids, and fatty acids (pp. 44-47).

Heptachlor-resorcinol, [Heptachlor-1,3-cyclohexandion],

CHCl < CCl₂ = CO > CCl₂, melting at 50° and boiling at 170° (25 mm.), is produced in the action of chlorine upon resorcinol in chloroform (B. 24, 912). Decomposition, p. 45.
Quinone Tetrabromide, [2,3,5,6-Tetrabromcyclohexandion],

CO CHBr. CHBr. CO (p. 168). Hexachlortriketo-R-hexylene, [Hexachlor-1,3,5cyclohexantrion], CCl₂CO">CCl₂CO">CO, melting at 48° and boiling at 268° (760 mm.), 150° (19 mm.), results from the action of chlorine upon phloroglucin in chloroform solution (B. 22, 1473). Decomposition—see p. 44.

Pentabromdiketo-oxy-R-hexene Hydrate, $CBr_2 < \frac{CO - CBr_2}{CO - CBr} > C. OH + H_2O$, melts at 119° with decomposition. It is produced when bromine in water acts upon phloroglucin. It forms amber-yellow-colored crystals. It is a strong acid.

Hexabromtriketo-R-hexylene, C₆Br₆O₃, melts at 147° (B. 23, 1729).

Tri- and Tetrachlortetraketohexamethylene, CCl₂<00-CO₂CCl₂, melt at 250° with decomposition, and at 60°. They are obtained from chloranilic acid and chlorine. The corresponding bromine derivatives are made from bromanilic acid (B. 25.

b. Ring-ketones from the Tetrahydrobenzenes can be synthesized by condensing acetoacetic ester, acetone dicarboxylic ester, and analogous compounds with aldehyde iodides, like methylene iodide, or with aldehydes in the presence of small quantities nythe totales, the methylene totale, or with attemptes in the presence of similar quantities of bases, such as diethylamine or piperidine, to 1,5-diketone-carboxylic esters—e.g., methylene-, ethidene-, isobutylidenediacetoacetic ester and methylenebisacetonedicuboxylic ester. When the latter are treated with hydrochloric acid in ether, they first form a ring and become carboxylic esters of Δ_g -keto-R-hexenes, and then, when acted upon with alkalies or dilute acids, are saponified, split off CO_g , and change to the ketones themselves (A. 289, 131):

3-Methyl-Δ₂-keto-R-hexene, boiling at 200°, is a mobile liquid with an agreeable odor. Its bromine addition product decomposes spontaneously into HBr and m-cresol. Its oxime melts at 63° and boils at 130° (18 mm.) (A. 288, 355).
3,5-Dimethyl-Δ-keto-R-hexene boils at 211°. Its dibromide changes quite readily

into sym. xylenol (p. 144) (A. 281, 121). 3,5,5-Trimethyl-Δ₁-keto-R-hexene, Isoacetophorone, *Isophorone*,

(CH₃)₃C CH₃. CO CH CH₃, boiling at 89°(10 mm.), is produced in the condensation of mesityl oxide with acetoacetic ester, saponification, and elimination of carbon dioxide from the carboxylic ester formed at first. It also results from the condensation of acetone by means of lime or sodium ethylate. It is isomeric with phorone (1, 221), camphorphorone (see this), and isocamphorone (see this). Upon reduction with sodium and alcohol it forms dihydroisophorol, $C_0H_{17}(OH)$, which by loss of water becomes trimethylcyclohexene, and by the reduction of its iodide yields trimethylcyclohexane. When oxidized with potassium permanganate the ring is ruptured and various acids result: $C_0H_{10}O_0$

C₈H₁₁O₃, and finally C₆H₁₀O₄, unsym. dimethylsuccinic acid (private communication from J. Bredt and Rübel, and E. Knövenagel; compare A. 290, 123).

3-Methyl-5-isopropyl-Δ₃-keto-R-hexene, C₂H₇. CH

CH₃. C(CH₃)

CH₄. CCH₄. CO

CH₅. C(CH₃)

CH₇. CH

CH₇. CH

CH₈. C(CH₃)

CH₇. CH

CH₈. C(CH₃)

CH₈. C(CH₃)

CH₈. C(CH₃)

CH₉. C(

3-Methyl-5-isobutyl- and 3-methyl-5-hexyl- Δ_{\bullet} -keto-R-hexene boil at 147° and at

167° (22 mm.) (B. 288, 336, 344).

Those chemists who consider the quinones to be ketones regard rhodizonic acid (p. 171) as a tetraketotetrahydrobenzene derivative.

Halogen substitution products of ring-ketones of tetrahydrobenzenes result when chlorine acts upon phenols, anilines, oxybenzoic acids, etc. They can be very readily torn asunder (pp. 44-47).

Heptachlorketotetrahydrobenzenes, CCl₂ CCl = CCl CHCl . CCl₂ CO and

CCl — CCl₂ CO, the α -body melting at 98° and the β -modification at 80°,

result from the action of chlorine upon m-chloraniline (B. 27, 547).

Octochlorketotetrahydrobenzene, CCl₂ CCl₂ CCl₂ CCl₃ CC, or

CCI CCl₂ CCl₂ CO, melting at 103°, result from the action of chlorine upon pentachlorphenol in glacial acetic acid, and from perchlor-m-oxybenzoic acid. Reducing agents change it into pentachlorphenol (B. 27, 550).

Hexachlor-o-diketo-R-hexene, $CCl_3 < \frac{CCl_2 - CO}{CCl} > CO + 2H_2O$, melts at 93° with decomposition. It is formed when chlorine acts upon pyrocatechol and o-amidophenol chlorhydrate dissolved in acetic acid. Stannous chloride reduces it to cyclobenzoquinone (p. 167). See p. 44 for its decomposition and conversion into a cyclopentene derivative. Homologous o-diketochlorides have been obtained from o-diamidomethyl benzenes (B. 27, 560).

Pentachlor-m-diketo-R-hexene, CCl CO — CCl₂ CO, melting at 92° and boiling at 160° (25 mm.), results when chlorine acts upon resorcinol in chloroform (B. 23, 3777). See p. 45 for its decomposition.

Hexachlor-m-diketo-R-hexene, CCl₂ CO — CCl₂ CO, melting at 115° and boiling at 159° (14 mm.), is produced when chlorine acts upon 3,5-dioxybenzoic acid dissolved in glacial acetic acid (B. 25, 2688).

Hexachlor-p-diketo-R-hexene, CO $< \frac{\text{CCl}_3}{\text{CCl}_3} = \frac{\text{CCl}_3}{\text{CCl}_3} > \text{CO}$, melting at 89° and boiling at 184° (45 mm.), is formed when chlorine acts upon p-amidophenol hydrochloride in

at 106°, we have chlorine derivatives of one or of both ketodihydrobenzenes. The first body is formed from trichlorphenol and chlorine, and the second, most conveniently, by heating (B. 27, 546) the heptachlorketotetrahydrobenzene, melting at 98°, and by treating phenol, anisol, and pentachloraniline with chlorine (B. 28, R. 63).

carvone, described after the terpenes, is very probably a ketodihydro-p-cymene.

Each of the possible dihydrobenzenes also yields a diketone:

If the diketone formula is preferred for the benzoquinones, previously discussed with the phenols (pp. 166-175), then p-benzoquinone is p-diketodihydrobenzene, and its numerous derivatives are also deducible from the latter compound. o-Benzoquinone would be o-diketodihydrobenzene. It is only known in its tetrahaloid substitution products, which were discussed under the benzoquinones before the para-quinones.

5. HYDROAROMATIC CARBOXYLIC ACIDS.

Attached to the hydroaromatic hydrocarbons, ring-alcohols, ringamines, and ring-ketones are numerous hydroaromatic carboxylic acids, their corresponding hydroaromatic alcohols, aldehydes, and ketones, which, however, have only been prepared in very special cases. In addition to the simple carboxylic acids, oxy- and keto-carboxylic acids are also known. Shikimic and quinic acids belong to the first class (p. 301), while in the second class we find succino-succinic ester (p. 305) and other important ketone-carboxylic esters, which are of great value in the synthesis of the simple hydroaromatic derivatives (p. 302).

1. HYDROAROMATIC MONOCARBOXYLIC ACIDS.

A (1). Hexahydrobenzoic Acids, Hexamethylene Carboxylic Acids, Nephthesic Acids, have been obtained by the reduction of boiling amyl or capryl alcohol solutions of benzoic acid and its homologues with metallic sodium, or by reducing the solution of sodium benzoate with sodium in an atmosphere of CO₂ (B. 24, 1865; 25, 3355). So far as present experience warrants they are isomeric and not identical (B. 27, R. 195, 197) with the "natural naphthenic acids" occurring in the oil which issues from the earth in and about Baku. Just as fatty acids have been prepared from malouic acids, so hexamethylene monocarboxylic acids have been obtained by heating hexamethylene-I,I-dicarboxylic acids (p. 202). The latter hodies have been prepared synthetically dicarboxylic acids (p. 302). The latter bodies have been prepared synthetically.

The hexamethylenecarboxylic acids are weak acids. They are reduced, when heated

with hydriodic acid, to hexahydroaromatic hydrocarbons—naphthemes, containing a like number of C-atoms in the molecule. Hence they are also designated as naphthemic acid. Hexahydrobenzoic Acid, Naphthenic Acid, C₂H₁₁. CO₂H, melting at 23° and boiling at 232°, results from the reduction of benzoic acid (see this), Δ₂-tetrahydrobenzoic acid (A. 271, 261), p-dimethylamidobenzoic acid (B. 27, 2829), and cyclobexanol-1-carboxylic acid (B. 27, 1231); also by heating hexamethylene-I, I-dicarboxylic acid. The calcium salt, (C,H₁₁O₂)₂Ca + 5H₂O. The methyl exter boils at 182°. The ethyl exter boils at 194°, and the amide melts at 185°.

> Hexahydro-o-toluic Acid melts at 51° and boils at 241°. Hexahydro-m-toluic Acid is a liquid, boiling at 245°. a-Hexahydro-p-toluic Acid melts at 110° and boils at 246°. β -Hexahydro-p-toluic Acid is a liquid.

These four acids have been obtained by the reduction of the three toluic acids (J. pr. Ch. [2], 49, 65; B. 27, R. 195). The last acid was also obtained by reducing $\Delta_{\mathbf{r}}$ -dibromtetrahydrotoluic acid, the addition product of 2HBr to p-methylenedihydrobenzoic acid (see this) (A. 280, 156), and hexahydro-o-toluic acid also from 2-methylhexamethylene-I, I-dicarboxylic acid (p. 302), and from 2-methyl-I-acetylhexamethylene-carboxylic ester (p. 302).

a Monobromhexahydrobenzoic Acid, melting at 63°, and a Monobromhexahydro-p-toluic Acid, melting at 71°, are produced by acting with bromine upon the chlorides of the corresponding hexahydro-acids.

Hexahydroanthranilic Acid, o-Amidohexahydrobensoic Acid, NH2[2]C3H10. CO2H, melts with decomposition at 274°. It is formed along with pimelic and hexahydrobenzoic acids in the reduction of anthranilic acid (B. 27, 2470; A. 295, 187). Hexahydrop-dimethylamidobenzoic Acid (B. 27, 2831).

Derivatives of o-amidohexahydrophenylacetic acid and propionic acid result in oxid-

izing dekahydroquinoline compounds with potassium permanganate. Octobydrocarbostyril, C_6H_{10} $\left\{ \begin{matrix} CH_2 & CH_2 \\ NH & CO \end{matrix} \right\}$, melting at 151°, is poisonous (B. 27,

A (2). Tetrahydrobenzoic Acids can be obtained from the a-monobromhexahydroacids (see above) by splitting off HBr with alkalies, or by means of quinoline (A. 271, 207; 280, 163), and also by the reduction of the benzoic acids and dihydrobenzoic acids (B. 26, 457).

CH₂ CH₃ . CH₃ C. CO₂H, is formed from a- Δ_1 -Tetrahydrobenzoic Acid, bromhexahydrobenzoic acid and from A4,6-dihydrobenzoic acid.

omhexanydropenzoic acid and noin ω₄, σταμγείουσε.

Δ₁. Tetrahydropenzoic Acid, Benzoleinic Acid, CH₂ CH₂ CH₃ CH₄ CH₅. is a liquid boiling at 234° (A. 271, 234; B. 27, 2471). It is formed from benzoic acid.

Δ. Tetrahydro-p-toluic Acid melts at 132°.

Isogeranic Acid, CH CH CH CH CO₂H (?), melting at 103° and $CH_2 - C(CH_3)_2$ boiling at 138° (11 mm.), results when geranic acid (1, 289; 11, 310) is acted upon with concentrated sulphuric acid (B. 27, R. 768).

A(3). Dihydrobenzoic Acids.—Δ4,6-Dihydrobenzoic Acid,

C. CO₂H, melting at 94°, is produced in the oxidation of dihydro-CH, CH, bensaldehyde, boiling at 121-122°, with silver oxide. The latter body is formed by decomposing anhydroecgonine-dibromide with sodium carbonate (B. 26, 454). A different dihydrobenzoic acid, melting at 73°, is obtained from Δ_2 tetrahydrobenzoic acid dibromide (B. 24, 2622). Dihydrocumic Acid, p-Isopropyldihydrobenzoic Acid, C₄H₄(C₅H₇)COOH, melting at 130-133°, is formed when nopic acid, an oxidation product of turpentine oil (see this), is boiled with sulphuric acid (B. 29, 1926).

B. Hexahydro-oxybenzoic Acids.—a-Oxyhexamethylene Carboxylic Acid, melting at 106°, is formed when cyclohexanon (p. 296) in ether is treated with prussic and hydrochloric acids; see also hexahydrobenzoic acid.

Hexahydrosalicylic Acid, (β-) Hexahydro-o-oxybenzoic Acid,

CH₂ CH₁ . CH(OH) CH . CO₂H, melting at 111°, results when nitrous acid acts **upon** hexahydroanthranilic acid and by reducing eta-ketohexamethylene-carboxylic ester (B. 27, 2472, 2476).

Hexahydro-m-oxybenzoic Acid, melting at 132°, is obtained by the reduction of

m-oxybenzoic acid with sodium in ethyl alcohol (B. 29, R. 549).

Hexahydro-dioxybenzoic Acid is obtained from Δ_1 -bromhexahydrobenzoic acid

(A. 271, 280).

Dihydroshikimic Acid, Hexahydrotrioxybenzoic Acid, (HO)3 C6H8. CO2H, melting at 175°, results when shikimic acid is reduced with sodium amalgam. Corresponding to it is Dibromshikimic Acid, (HO)₃C₄H₄Br₂. CO₂H, which upon evaporation with water changes to a brom-lactone, C₂H₃BrO₅, melting at 235°.

Quinic Acid, Hexahydro-tetraoxybensoic Acid, (HO)₄. C₆II₇. CO₂II, melting at 162°, optically active, is present in the cinchona barks, in coffee beans, in bilberry, and in many other plants. It is obtained as a secondary product in the preparation of quinine by extracting the quinia bark. When its calcium salt has been purified by recrystallization the acid is liberated by oxalic acid. Upon distillation the acid breaks down into phenol, hydroquinone, benzoic acid, and salicylaldehyde. When boiled with water and lead peroxide it changes to hydroquinone, while manganese peroxide and sulphuric acid convert it into quinone (p. 167). Protocatechuic acid is formed when it is melted with caustic potash or soda (p. 227). Ferments decompose calcium quinate into protocatechnic acid. If the fermentation takes place with air exclusion the products are formic acid, acetic acid, and propionic acid. Quinic acid is reduced by hydriodic acid to ben**zoic acid.** The calcium salt has the formula $(C_7H_{11}O_6)_7Ca + 10H_2O$. ethyl ester, $C_9H_7(O.C)CH_3)_4$. $CO_2C_2H_5$, melts at 135° (B. 22, 1462). The tetracetyl-

Inactive Quinic Acid is produced when its lactone, quinide, is boiled with milk of

Calcium salt, (C₇H₁₁O₆),Ca + 4H₂O. lime.

Quinide, C₁H₁₀O₅, melting at 198°, optically inactive, results upon heating ordinary optically active quinic acid to 220-240° (B. 24, 1296).

Dioxydinydroshikimic Acid, Hexahydro-pentaoxybenzoic Acid, (110), CaHa. COaH, melts at 156° with the elimination of water. It is optically inactive and is obtained from the brom-lactone, melting at 235°, which is formed in the action of baryta-water (B. 24, 1294) upon dibromshikimic acid (see above).

Shikimic Acid, Trioxytetrahydrobenzoic Acid, (HO)3C6H6. CO2H, melting at 184°, occurs in the fruit of Illicium religiosum (see shikimol, p. 270). Its transposition products, dihydro- and dioxydihydroshikimic acids, have been previously described.

C. Ketohydromonocarboxylic Acids.—(o-) β -Ketohexamethylene Carboxylic.

Ester, CII₂. CO₂. CO₃. CO₃R, is formed when pimelic acid ester is heated with sodium and alcohol (B. 27, 103).

(m·) . Ketohexamethylene Carboxylic Acid, CH₂ < CO . CH₂ > CH . CO₂H, is produced when tetrahydro-oxyterephthalic acid is heated to 115°, or boiled with water, or when m oxyhexahydrobenzoic acid, in the form of its ester, is oxidized with sodium bichromate (B. 29, R. 550).

2-Methyl-I-acetylhexamethylene Carboxylic Ester,

 $CII_2 < \frac{CH_2 - CII(CH_2)}{CII_2 - CII_2} > C < \frac{CO_2C_2H_3}{CO.CH_2}$, is obtained from methylpentamethylene dibromide and sodium acetoacetic ester. On boiling with alcoholic potash it breaks down into 2-methylhexamethylene carboxylic acid, or hexahydro-o-toluic acid (p. 300) and methylhexamethylenemethyl ketone, 2-Methylhexahydroacetophenone, boiling at 197-200° (B. 21, 737).

3-Methyl-A2-keto-R-hexene-6-carboxylic Ester,

CH₃. CCH₂ CH₂ CH₃ CH₄ CCH₃ CCH₄ CCO₂C₂H₅], boiling at 151° (22 mm.), is produced from the interaction of methylene iodide and accessetic ester in a form soluble in alkali and a form insoluble in alkali (keto- and hydroxyl?). The neutral ester is changed by treatment with sodium ethylate in ether into the sodium salt of the ester soluble in alkali. Both esters, when treated with sodium alcoholate and isopropyl iodid**e, yield**-

3,6 Methylisopropyl- 2-keto-R-hexene-6-carboxylic ester, boiling at 158° (18 mm.). The corresponding keto-R-hexene (p. 298) (B. 30, 639) is obtained from this ester by

saponification and the splitting-off of carbon dioxide.

2. HYDROAROMATIC DICARBOXYLIC ACIDS.

A. Hexahydrodicarboxylic Acids.—These acids, depending upon the position of the carboxyl groups with reference to one another, show the deportment of dialkyl malonic acids, sym. dialkylsuccinic acids, sym. a-dialkylglutaric acids, and sym. a-dialkyladipic acids.

Hexamethylene-1,1-dicarboxylic ester and 2-Methylhexamethylene-1,1-dicarboxylic ester have been made by the action of sodium malonic ester upon pentamethylene bromide and methyl-pentamethylene bromide. The free acids, when heated, split off CO, and become hexahydrobenzoic acid and hexahydro-o-toluic acid. 2-Methylhexamethylene-1,1-dicarboxylic Acid, CH₂ < CH₂ . CH₃ . CH₃ CC(CO₂H)₂, melts at 147°. Hexamethylene dicarboxylic acid and its esters appear not to have been isolated

as yet (B. 21, 735; 26, 2246). Hexahydrophthalic Acids.—A. Baeyer's theory (B. 23, R. 577), based upon the spacial representations of van t'Hoff as to the union of the C-atoms, predicts the possibility of geometrically isomeric hexahydrophthalic acids. The latter isomerism is due to

the different positions occupied by the carboxyls relatively to the plane of the hexamethylene ring; hence the isomerides are termed cis and trans forms.

cis-Hexahydro o-phthalic Acid, 1,2-Hexamethylenedicarboxylic Acid, CoH10(CO, II), melts at 192° and its anhydride melts at 32° and boils at 145° (18 mm.); the trans-Hexahydro-o-phthalic Acid melts at 215° and its anhydride at 1.0°. They are produced together when Δ_1 -tetrahydro-o-phthalic acid is reduced. The cis-acid is more soluble in water than the trans-acid. The anhydride of the latter is converted by continuous heating at 210-220° into the anhydride of the cis-acid (A. 258, 214).

Hexahydro-isophthalic Acids are produced in the reduction of isophthalic acid and when 1,1,3,3-hexamethylenetetracarboxylic acid is heated to 200-220°. The calcium salt of the cis-acid is more sparingly soluble. The cis-acid, melting at 162°, when heated to 180° with hydrochloric acid, changes in part to the trans-acid, melting at 188°. Both acids, with acetyl chloride, yield the acid anhydride, melting at 119° (B. 26, R 721).

Hexahydroterephthalic Acids result on reducing the hydrobromides of the tetrahydroterephthalic acids in glacial acetic acid with zinc-dust, as well as upon heating hexamethylene-1,1,4,4-tetracarboxylic acid to 200-220°. In the latter case the trans-acid, melting at 200°, predominates. The cis-acid, melting at 161°, is also converted into it when heated with hydrochloric acid to 180°. As far as concerns solubility, these three pairs of hexahydrophthalic acids reduce fumaric and maleic acids. They are also convertible one into the other in like manner. They have also been distinguished, one from the other, as maleinoid and fumaroid modifications.

a-Brom-substitution products of these acids have also been prepared from the acid chlorides by treatment with bromine. Brom-substituted hexahydrocarboxylic acids have also been obtained by the addition of hydrogen bromide and bromine to the corresponding tetra- and dihydrodicarboxylic acids.

B. Tetrahydrodicarboxylic Acids, Tetrahydro-o-phthalic Acids.—Depending upon the point of double union there are, theoretically speaking, four structurally isomeric bodies. The two modifications in which neither of the two CO₃H groups are attached to a doubly combined C-atom permit of a stereoisomeric modification each.

CH₂. CH₃. C. CO₃H melting at 120° and its Δ_1 -Tetrahydro-o-phthalic Acid, anhydride at 74°, is formed when hydropyromellitic acid is distilled (p. 307). Potassium permanganate decomposes it into adipic acid (A. 166, 346; 258, 203).

CH₂ CH = C. CO₂H

Δ₃.Tetrahydro-o-phthalic Acid, cH₂—CH₂—CH₂—CH₂ cH₁ melting at 215° and its anhydride at 78°, has been obtained by the decomposition of sedanonic acid (B. 30, 503). It is also formed on boiling the Δ_1 -acid with caustic potash, when the double union is shifted, and by the reduction of phthalic acid or Δ_{216} -dihydrophthalic acid CH_CH_CH.CO,H together with trans-A. Tetrahydro-o-phthalic Acid,

CH . CH, . CH . CO₂H at 216° and its anhydride at 140°. Acetyl chloride separates it from the Δ_2 -acid.

reagent converts it alone into its corresponding anhydride (A. 258, 211).
cis Δ₄-Tetrahydro-o-phthalic Acid melts at 174°. It is produced when the

 $\Delta_{2,4}$ -dihydro-acid is reduced, as well as from its anhydride, melting at 58°. The latter anhydride is formed when the anhydride of the trans- Δ_4 -acid is heated (A. 269, 202).

Tetrahydro-terephthalic Acids are theoretically possible in two structurally isomeric forms, depending upon the position of the double union; one of these can occur in two stereoisomeric modifications.

 Δ_j . Tetrahydro-terephthalic Acid, CO₂H. CH<CH $_2$ CH $_3$ CH $_4$ CH $_5$ CH. CO₂H, is produced in two isomeric modifications by the reduction of $\Delta_{1:9}$ and $\Delta_{1:9}$ dihydrotered to the control of $\Delta_{1:9}$ CH $_4$ CH $_5$ CH $_$ phthalic acids. The trans-acid melts at about 300°. The cis-acid melts at 150°. The latter is much more readily soluble in water than the former. Potassium permanganate oxidizes them to succinic acid. Boiling sodium hydrate changes the two acids, like

oxidizes them to succinic acid. Doning social 1,467). β_{J} -hydromuconic acid, into $a\beta$ -hydromuconic acid (1,467). $CH_{3}-CH$ Δ_{1} -Tetrahydro-terephthalic Acid, $CO_{2}H$. CH $CH_{2}-CH_{3}$ $C \cdot CO_{3}H$, melts

beyond 300° and sublimes (A. 258, 7).

C. Dihydrocarboxylic Acids.—Dihydro o-phthalic Acids are possible, according to the position of the double union, in six structurally isomeric forms, one of which can occur in two stereoisomeric modifications.

 $CH \cdot CH_{\bullet} \cdot C \cdot CO_{\bullet}H$ dride at 134°), is produced on boiling A2,4 dihydrophthalic acid with acetic anhydride (A. 269, 204).

CH. CH₂. CH. CO₂H Δ. Dihydro-o-phthalic Acid, , melting at 179° (its anсн. сн. с. со,н hydride at 103°), is produced when the acid is acted upon in the cold with acetic anhydride. The acid is produced, further, on boiling Δ_{200} -dihydro-o-phthalic acid dihydro-bromide with methyl alcoholic potash.

 Δ_{24} -Dihydro-o-phthalic Acid, CH_2 . $CH: C: CO_2H$ melts at 215° and its easy-dride at 83°. The acid results by reducing phthalic anhydride with sodium amalgam in alkaline solution, and by boiling the Δ_{24} - and Δ_{246} -acid with sodium hydrate (see also B. 27, 3185).

trans- $\Delta_{3,5}$ -Dihydrophthalic Acid, CH: CH. CH. CO₂H CH: CH: CO₂H, melting at 210°, is produced by reducing phthalic anhydride with sodium amalgam in acetic acid solution.

cis 4,5 Dihydrophthalic Acid melts at 174°. Its anhydride, melting at 99°, is

formed when the trans- $\Delta_{3\cdot5}$ -acid is acted upon with acetic anhydride.

Dihydroterephthalic Acids.—Depending upon the points of double union, there are four possible structural isomerides. One of these, the \triangle_{215} -acid, appears in two stereoisomeric forms. All the modifications are known.

CH . CH $\Delta_{1/2}$ -Dihydroterephthalic Acid, CO₂H . CH₂ . CO₂H, is produced on digesting a, a_1 -dibromhexahydroterephthalic acid and Δ_1 tetrahydroterephthalic acid dibromide with alcoholic potash (A. 258, 23). The directly lester melts at 85°.

 $\Delta_{1:4}$ -Dihydroterephthalic Acid, CO₂H . CH₂ . CH₂ . CO₂H, is formed by reducing terephthalic acid with sodium amalgam, by boiling the isomeric dihydroterephthalic acids with sodium hydrate (A. 251, 272), and by reducing p dichlor- $\Delta_{1:4}$ -dihydroterephthalic acid with sodium amalgam (B. 22, 2112).

The dimethyl ester melts at 130°.

p Dichlor Δ_{14} dihydroterephthalic Acid, $C_8H_6Cl_2O_4$, melts at 272-275° with decomposition. It results upon treating succino-succinic ester with PCl₅ (B. 22, 2106).

 $\Delta_{1.5}$. Dihydroterephthalic Acid results on boiling trans $\Delta_{2.5}$ dihydroterephthalic acid with sodium hydroxide; the *dimethyl ester* resinifies on exposure to the air (A. 258, 18).

 $\Delta_{2.5}$ -Dihydroterephthalic Acids, CO_2H . CH < CH: CH > CH. CO_2H , cis-acid and trans-acid, are formed in the reduction of terephthalic acid. See also $\Delta_{1.5}$ -dihydroterephthalic acid. The trans-diphenyl ester melts at 146°. The cis-dimethyl ester melts at 77° (A. 258, 17).

D. and E. Oxy- and Ketohydrobenzene Dicarboxylic Acids.—a-Oxy-hexa-hydroisophthalic Acid, CH₂—CH₂—CH₂—CO₂H, is obtained from m-keto-hexa-hydrobenzoic acid by the action of prussic acid and hydrochloric acid (B. 22, 2186).

Dicarboxylic Acid CH — CH₂—C(OH)——CO₂H

m Dioxyhexahydroisophthalic Acid, CII₂ CH₂—C(OH)——-CO₂H composition at 217°. Its anhydride melts at 175°. The acid is obtained from its nitrile, the product of the addition of prussic acid to dihydroresorcinol (p. 297) (A. 278, 49).

a,a₁-Dioxyhexahydroterephthalic Acid, $\stackrel{CO_1H}{HO}$ C $\stackrel{CH_2-CH_2}{CH_2-CH_2}$ CC $\stackrel{CO_1H}{OH}$, is formed when its cyanide, melting with decomposition at 180°, is boiled. This cyanide results by adding prussic acid to p-diketohexamethylene with hydrochloric acid (B. 22, 2176).

 Δ_1 -Tetrahydro-2-oxyterephthalic Acid, or 2-Ketohexamethylene-1,4-dicarboxylic Acid,

CO — CH₂ CH . C(OH) C . CO₂H, or CO₂H . CH CH₂ CH . CO₂H, cresults from the reduction of oxyterephthalic acid (p. 243). When heated to 60° with water, it splits off carbon dioxide and becomes m-ketohexahydrobenzoic acid (p. 304),

the oxime of which is obtained from tetrahydro-oxyterephthalic acid by means of hydroxylamine hydrochloride (B. 22, 2178).

Tetrahydro-dioxyterephthalic Acid-p. 243.

Ketotetrahydrobensene polycarboxylic esters and m-diketohexahydrobensene carboxylic esters or hydro-resorcylic esters have been prepared synthetically in great numbers from 1/5-diketone- and d-ketone carboxylic esters respectively by the elimination of water or of alcohol. A series of keto-R-hexenes, dihydroresorcinols, tetrahydrobenzenes, dihydrobenzenes, etc., has been built up from these bodies as the starting out substances (pp. 297, 298).

Succino-succinic Acid, CO, H. CH < CO. CH, CO, CH. CO, H, results upon saponifying its diethyl ester with a calculated amount of normal sodium hydroxide, and by treating 2,5-dioxyterephthalic ester with sodium amalgam. The dry acid breaks down into two molecules of carbon dioxide and p-diketohexamethylene when heated to 2000 (B. 22, 2168).

Succino-succinic Diethyl Ester, melting at 126°, is produced by the condensation of two molecules of succinic ester through the agency of potassium, sodium, or sodium ethylate upon succinic ester (A. 211, 306) or bromacetoacetic ester (A. 245, 74), as well as by the interaction of silver cyanide and iod-acetoacetic ester (A. 253, 182), and by the reduction of 2,5-dioxyterephthalic ester with zinc and hydrochloric acid (B. 19, 432).

Succino succinic ester behaves like phloroglucin. It also manifests many reactions of a ketone, corresponding to formula I of 2,5-diketohexamethylene carboxylic ester; whereas it also conducts itself like a phenol, corresponding then to formula II of 2,5dioxydihydroterephthalic ester (B. 24, 2692):

The ester crystallizes in bright green triclinic prisms or colorless needles. It is insoluble in water, dissolves with difficulty in ether, very readily in alcohol; its solution shows a bright blue fluorescence. Ferric chloride imparts a cherry red color to it. It dissolves in alkalies with a yellow color, yielding metallic derivatives by the replacement of two hydrogen atoms. It does not unite with phenylisocyanate.

With hydroxylamine (in alkaline or acid solution) succino-succinic ester splits off CO. and yields quinone-dioxime carboxylic ester, C. H. (N. OH)2. CO2R, melting at 1740

With phenylhydrazine it forms a phenylhydrazine derivative of dihydroterephthalic acid (B. 24, 2687; 26, R. 590), while with hydrazine it yields hexahydrobenzo-3,4dipyrazolon (see this) (B. 27, 472). Also consult dichlordihydroterephthalic acid.

If succino-succinic ester be saponified by dilute alkalies, with exclusion of air, it yields

free

Succino-succinic Dimethyl Ester, melting at 152°.

The following compounds are produced as the result of the interaction of sodium succino-succinic diethyl ester and alkyl iodides (B. 26, 232):

Diethyl Succino-succinic Ester: cis-body is liquid; trans-body melts at 65°. Di-n-propyl Succino-succinic Ester: cis-body is liquid; trans-body melts at 86°. Di-isopropyl Succino-succinic Ester: cis-body is liquid; trans-body melts at 116°.

Methyl-n- and Methylisopropyl Succino-succinic Ester boil at 195-200° (25

mm.); see dihydro-p-cymene, p. 294.
p-Dichlorquinone Dicarboxylic Ester, C₆Cl₂O₂(CO₂C₂H₆)₂, melting at 195°, consists of yellowish green crystals (B. 21, 1761). When reduced with zinc-dust and glacial acetic acid it becomes p-Dichlorhydroquinone-dicarboxylic Ester, CaClaHa-O2(CO2C2H5)2, crystallizing in two different forms—colorless needles and yellow green plates (B. 20, 2796; 21, 1759; 23, 260). Compare the two forms of 2,5-dioxyterephthalic ester, p. 243.

p-Dloxy-quinone-dicarboxylic Ester, C₆O₂(OH)₂(CO₃C₂H₈)₂, melting at 151°, may be prepared by shaking dichlorhydroquinone-dicarboxylic ester with sodium hydroxide, and by the action of nitrous acid upon dioxy-terephthalic ester (B. 19, 2385). It crystallizes in pale yellow leaflets and intense greenish-yellow prisms (B. 20, 1307). Note above, p-dichlorhydroquinone-dicarboxylic ester, and see p. 243. It reacts acid, and forms salts with two equivalents of the metals. It does not form a dioxime with hydroxylamine, but an oxyammonium salt, and with phenylhydrazine a phenylhydrazine salt (B. 22, 1290). Furthermore, it does not react with phenylcyanate (B. 23, 265). Boiling hydrochloric acid decomposes the ester into carbon dioxide and dioxy-quinone (p. 170). By the absorption of two atoms of hydrogen (by reduction with sulphurous acid) the ester becomes-

Tetroxy-terephthalic Ester, $C_0(OH)_0(CO_2R_2)$, or Dioxy-quinone-dihydrocarboxylic Ester, $C_0(H)_0(CO_2R)_2$. It crystallizes in golden yellow leaflets and melts at 178° (B. 20, 2798). Its alkaline solution oxidizes on exposure to the air (giving up two hydrogen atoms) to dioxy-quinone-dicarboxylic ester; hence it yields the same products with hydroxylamine and phenylhydrazine (B. 22, 1291). It forms a tetracarbanilido derivative (B. 23, 267) with four molecules of phenylcyanate.

1,3,5-Triketohexamethylene Dicarboxylic Ester, C₆H₄O₈(CO₂C₂H₅)₃, melting at

1010, results from the condensation of acetone dicarboxylic ester and malonic ester with

sodium ethylate (B. 29, R. 1117).

3. Hydrobenzene Tricarboxylic Acids.—This group probably includes dioxyphenylacetic dicarboxylic triethyl ester, CH₂ CO—C(CO₂C₂H₅) C.CH₂·CO₂C₁H₅ or CO₂C₃H₅CII CO-CH₂ CO-C(CO₂C₃H₅) C.CII₂.CO₂C₃H₅ (pp. 44, 229), and a similarly

prepared body-Phloroglucin Tricarboxylic Ester, CO_2 . C_2H_5 . $CH < CO - CH(CO_2C_2H_5) > CO$,

melting at 104°. It may be formed by the condensation of malonic ester upon heating its sodium compound to 120-145°, or by the action of zinc ethyl. It deports itself quite like succino-succinic ester, dissolves unchanged in alkalies, and is colored a cherry-red by ferric chloride. Acetic anhydride converts it into a triacetyl derivative, and with hydroxylamine it yields a trioxime (B. 21, 1766); with phenyl cyanate it forms a tricarbanilido derivative (B. 23, 270). Fused with alkalies it forms phloroglucin.

4. Hydrobenzene-tetracarboxylic Acids.—Acids having two carboxyl groups attached to the same carbon atom have been obtained synthetically in the action of trimethylene bromide upon the disodium compound of methylene dimalonic ester, as well as from the interaction of methylene iodide and disodiumtrimethylene dimalonic ester: hexamethylene-I,I,3,3-tetracarboxylic ester, and from n-butanetetracarboxylic ester with ethylene bromide: hexamethylene-I,I,4,4-tetracarboxylic ester (Perkin, Jr.; see p. 20);

1,1,3,3-Hexamethylenetetracarboxylic Acid decomposes at 220° with the elimination of 2CO2 into hexahydroisophthalic acid (B. 25, R. 159, 274).

1,1,4,4-Hexamethylenetetracarboxylic Acid, melting at 152-153°, yields, at more elevated temperatures, both hexahydroterephthalic acids; the trans-acid predominates

(p. 302).

Tetra-hydro- and iso-tetra-hydro-pyro-mellitic Acids, C₆H₂(H₄)(CO₂H)₄, are nium pyromellitate. The first results as a gummy mass upon evaporating the ethereal

solution; it is very soluble in water. The second crystallizes with 2H2O, loses the same about 120°, melts near 200°, and decomposes into water, carbon dioxide, and Δ_1 -tetrahydro-o-phthalic anhydride (p. 303) (A. 258, 205). When heated with sulphuric acid both evolve CO₂ and SO₂ and form trimellitic and isophthalic acids.

Quinone-tetrahydro-tetracarboxylic Ester, or p-Diketohexamethylene-tetra-CO₂. C₂H₅. CH — CO — CH . CO₂. C₂H₅ melts at 142-144°, when CO₂. C₂H₅ . CH — CO — CH . CO₂. C₂H₅

It is formed in the reduction of hydroquinone-tetracarboxylic ester (p. it is anhydrous. 246), the reduction product arising from quinone-tetracarboxylic ester (p. 246), zincdust, and hydrochloric acid in alcoholic solution. It crystallizes from alcohol in colorless meedles or prisms. Its deportment is perfectly analogous to that of succino-succinic ester. Ferric chloride imparts a cherry-red color to its alcoholic solution. Bromine changes it again to hydroquinone-tetracarboxylic ester (B. 22, R. 289).

Tetrahydroprehnitic Acid, $C_8H_8(CO_2H)_8$, is formed when sodium amalgam acts

upon an ammoniacal solution of prehnitic acid (p. 246). It is an amorphous mass, very readily soluble in water. It yields prehnitic and isophthalic acids when it is heated with

sulphuric acid.

5. Hexahydrobenzene-hexacarboxylic Acids.—Hexahydromellitic Acid, C₆H₄-(COOH), is produced when sodium amalgam acts upon ammonium mellitate. It is very soluble in water and crystallizes with difficulty. It melts with decomposition when it is heated. Its calcium salt is more easily soluble in cold than in hot water. When heated to 180° with concentrated hydrochloric acid, and also when it is preserved, it passes into isomeric-

Isohexahydromellitic Acid, C₆H₆(CO₂H)₆, which crystallizes in large hexagonal

prisms. It is precipitated from its salt solutions by hydrochloric acid.

Ring-formation of Hydroaromatic Compounds from Aliphatic Compounds.-The following hydroaromatic bodies have been synthetically prepared from aliphatic compounds:

1. Hexahydrobenzene (p. 292).

2. m-Dihydroisoxylene (p. 294).

3. Pimelin-ketone, Ketohexamethylene, and homologues (p. 296).

4. Trimethylketo-R-hexene or Isoacetophorone (p. 298).

Dihydroresorcinol and homologues (p. 296).
 β-Ketohexamethylenecarboxylic Ester (p. 301).
 2-Methyl-1-acetylhexamethylenecarboxylic Ester (p. 301).

8. 3-Methyl-A-keto-R-hexené-6-carboxylic Ester and homologues (pp. 298, 302, 305).
9. Hexamethylene-1,1-dicarboxylic Ester and homologues (p. 302).

10. m Diketohexahydrobenzene-carboxylic Ester (p. 305).

11. Succino-succinic Ester (p. 305).

- 12. Dioxyphenylaceto-dicarboxylic Ester (p. 306). 13. Phloroglucin Tricarboxylic Ester (p. 306).
- 14. Hexamethylene-1,1,3,3-tetracarboxylic Ester (p. 306).
- 15. Hexamethylene-1,1,4,4-tetracarboxylic Ester (p. 306).

TERPENES.*

The volatile or ethereal oils, obtained mostly by the distillation of various plants (chiefly Coniferæ and Citrus species) with steam, more rarely by pressing them out, contain, along with different compounds, certain hydrocarbons having the formula C₁₀H₁₆, which are called Terpenes. prene, C₄H₈, obtained by the distillation of caoutchouc, has the same percentage composition; it is a hemiterpene. There are also hydrocarbons

^{*} Fr. Hensler, "Die Terpene." 1896. Verlag von F. Vieweg u. Sohn, Braunschweig.

known having the formula C15H24; these are the sesquiterpenes, and there

are also higher polymerides, $(C_0H_0)x$, the polyterpenes.

The "true terpenes," $C_{10}H_{10}$, the important and often the chief components of many ethereal oils of great value in perfumery, demand particular attention. They contain one, and some of them probably two carbon rings. They are more or less closely related to cymene or p-isopropyl methyl benzene (p. 56). In recent years terpenes have also come to light which do not have a closed carbon chain; they are distinguished from the true terpenes as olefine terpenes.

Their classification and the possibility of distinguishing the individual true terpenes are mainly due to the painstaking researches of O. Wallach, who has brought order and system out of this chaotic mass of hydrocar-

bons of the most varying origin.

The question as to the constitution of the true terpenes has not yet been entirely settled as to any representative of this group of bodies.

They can, however, be arranged into two sub-groups.

Camphene, obtained from bornyl chloride, is a terpene. It probably continues to hold the carbon skeleton of camphor (p. 327). They are and pinene are related to it. These are three cyclic terpenes. only capable of adding two univalent atoms or atomic groups. cyclic terpenes of the limonene and pentene group are distinguished from the preceding bodies chiefly by their power of adding four univalent atoms. In this class we find hydrocarbons similar to the synthetically prepared p-dihydrocymene (p. 294). These cyclic hydrocarbons of the formula C₁₀H₁₆ may be called hydroaromatic terpenes in contradistinction to the camphenes, C10H16. Individual members of both groups are genetically allied to one another by certain transition-reactions. All of the true terpenes are unsaturated hydrocarbons; by the addition of hydrogen they become hydroterpenes.

The hydroterpenes give rise to a great number of alcohols and ketones, comprised under the general name camphor. In this class are included menthone, mentha camphor, and common or Japan camphor, a ketone of dihydrocamphene. The terpene alcohols and terpene ketones, with their transposition products, attach themselves naturally to the terpenes and their addition products.

Properties.—The true terpenes, when pure, are colorless, strongly refracting liquids.

Camphene alone is a solid.

They boil without decomposition at 155-180°. They are very volatile with steam and have a pleasant odor. Many are optically active. Some, indeed, exist in two optically active forms with equal but opposite rotatory power. Dipentene is a racemic terpene.

Department.—(1) Some terpenes polymerize very readily. (2) Boiling dilute alcoholic sulphuric acid has rearranged various terpenes into isomeric terpenes. (3) Many are oxidized by the oxygen of the air; they then manifest a tendency to resinify (see B. 29, R. 658). The formation of benzene derivatives by oxidizing terpenes is very important. Thus, turpentine oil with iodine yields cymene; with nitric acid, p-toluic acid and terephthalic acid. (4) The addition-reactions have already been pointed to as a means of classifying the terpenes. The terpenes capable of adding four hydrogen atoms are in all probability dihydrocymenes (see above). For the constitution of the camphene adding but two hydrogen atoms consult p. 327. (5) The addition of chlorine and bromine, as well as hydrogen halides, in glacial acetic acid at low temperatures gives rise to haloid hydroterpenes. Conversely, when the hydrogen halide addition-products are heated with sodium acetate in glacial acetic acid, or when heated with bases like aniline, the terpenes are regenerated. It is by means of these haloid bodies that the transition from

the terpenes into camphor alcohols can be realized. (6) Nitrosyl chloride, NOCl (Tilden), or an alkyl nitrite, glacial acetic acid, and hydrochloric acid acting upon ter-penes give rise to well-defined terpene nitroso-chlorides. These form terpene nitrolamines with primary and secondary bases, or, by splitting off hydrochloric acid, they become nitroso terpenes. v. Baeyer (B. 28, 648; 29, 10) contends that these nitrosochlorides are frequently to be regarded as bimolecular, and better as bisnitrosochlorides. (7 a) Several terpenes unite with N₂O₄, forming nitrosates, C₁₀H₁₆(NO). O. NO₂, (b) and with N₂O₃, yield nitrosites, C₁₀H₁₆(NO). O. NO. See B. 29, 695, for the addition of trichloracetic acid to the terpenes.

Nomenclature. - Baeyer, observing the "Geneva nomenclature," suggested that the cyclic terpenes containing the same carbon skeleton as p-cymene, the dihydro-pcymenes, be called Terpadiënes; then the tetrahydrocymenes would be terpenes and hexahydrocymene terpan. Camphene would retain its name, but dihydrocamphene would receive the name camphan: consequently, the terpenes can be divided into the terpan and camphan groups. To obtain names for the terpenes which would be designated, according to this suggestion, as terpadienes, Wagner calls hexahydrocymene menthan, the tetrahydrocymenes menthenes, and the dihydrocymenes or terpenes menthadiēnes (B. 27, 1636 Anm.).

The terpenes will, therefore, be discussed in three groups:

A. Olefinic Terpene- or Terpenogen Group.

B. Terpan or Menthan Group. C. Camphan Group.

The alcohols and ketones, the so-called camphors, attach themselves to the hydrocarbons of each group.

A. OLEFINIC TERPENE- OR TERPENOGEN GROUP.

Many olefine hydrocarbons, alcohols, aldehydes, and acids with open carbon chain are included under this designation. They occur in ethereal oils, or in the transposition products obtained from the latter. They are distinguished chiefly by the fact that they, as a rule, are easily converted into hydroaromatic, terpene-like, or aromatic substances.

1. Olefinic Terpenes: Myrcene, $C_{10}H_{16}$, boiling at 67° (20 mm.), sp. gravity 0.8025 (15°), $n_D = 1.4673$, occurs with l-phellandrene and the aromatic phenols of the cinnamic series in bay-oil. It can take up six atoms of bromine, and by the addition of hydrogen becomes linalcol. Anhydrogeraniol, C₁₀II₁₆, boiling at 172-176°, sp. gr. 0.8232 (20°), $n_D = 1.4835$, and obtained by heating geraniol with potassium sulphate to 170°, can also take up six bromine atoms (B. 24, 682). Linaloolene, $C_{10}H_{18}$, boils at 165-168°. Its sp. gravity is 0.7882 (20°), $n_D = 1.455$. It is formed in the reduction of linalool (B. 27, 2520).

Isoprene, C₅H₈, boiling at 37°, must be considered under the olefinic terpenes or ter-It is a distillation product from caoutchouc (p. 311). It very probably consists in the main of methyldivinyl, $\frac{\text{CII}_2}{\text{CH}_2}$ $C - C = \text{CII}_2$. It can take up two molecules of hydrogen bromide, forming dimethyl-trimethylene bromide. It polymerizes very readily to dipentene (p. 311) (J. pr. Ch. [2], 55, 1):

$${}^{2}CH_{3}$$
 C — CH = CH_{3} — CH_{3} C — CH CH_{2} — CH_{3} CCH_{3}

2. Olefinic Terpene Alcohols: Rhodinol, C₁₀H₂₀O, boiling at 113-114° (15 mm.), occurs, together with geraniol, in different rose, geranium, and pelargonium oils. Very probably it must be viewed as the optically active levorotatory alcohol, corresponding to citronellal: 1-citronellol, (CH₃)₂. C: CH. CH₂. CH₂. C(CH₃)H. CH₄. CH₄OH (B. 29, 923 ff.; 30, 33; compare B. 29, R. 785). Geraniol, C₁₈H₁₈O == (CH₂)₂C: CH. CH₂. CH₂. C(CH₃): CH. CH₂OH, boiling at 120-122° (17 mm.) constitutes the alcoholic constituent of geranium oil, rose oil, pelar-500 joint oil, etc. (B. 29, 785). It is optically inactive, and bears the same relation to modinol that citral sustains to citronellal.

1-Linalool, $C_{10}II_{18}O = (CH_2)_2C:CH.CH_2.CH_2.C(CH_3)OH.CH:CH_4$, boiling at $197-199^\circ$, sp. gr. 0.8702 (20°), $n_D = 1.4695$, is found in oil of lavender, bergamot, limet, and origanum. d-Linalool, coriandrol, occurs in the oil of coriander. Dilute sulphuric acid converts the linalool with ease into inactive terpine hydrate (p. 314);

this conversion is made with greater difficulty with geraniol (B. 28, 2137).

The constitution of these bodies, as well as that of the corresponding aldehydes and acids, has been mainly deduced from their conversion into methyl heptenone, (CH₂)C: CII. CH₂. CH₂. CO. CII₃, which has been previously described. Again, this methyl heptenone has been employed in the synthesis of certain bodies belonging in this group. Thus, by condensation with zinc and allyl iodide it yields homolinalool, (CH1), C: CH.

CH₂. CH₂.CH₃.OH. CH₃. CH: CH₄, boiling at 102-104° (14 mm.) (B. 29, 693).

Another series of olefinic terpene alcohols—e.g., licarcol, reuniol, ylangol—has been prepared from various ethereal oils. Their constitution has not yet been determined; probably they are identical with the compounds just described, or they are closely related

to them (B. 27, R. 505, 751; 28, R. 67).

3. Olefinic Terpene Aldehydes: Citronellal (Rhodinal?) (B. 29, R. 352), C₁₈H₁₀O = (CH₃)₂C:CH. CH₂. CH₃. C(CH₃)H. CH₄. CHO, boiling at 103-105° (25 mm.), is optically dextrorotatory. It is found in citronella oil, in the oil from Eucalyptus maculata, var. citriodora, etc. (B. 29, 904). Acetic anhydride condenses it to isopulegol, a terpene alcohol very similar to, yet not identical with, pulegol, a reduction product obtained from

pulegon (p. 320) (B. 30, 22). It changes to d-citronellol (see this) upon reduction. Citrel, Geranial, C₁₀H₁₆O = (CH₃)₂C: CH. CH₂. CH₃. C(CH₃): CH. CHO, boiling at 224-228°, is formed in the oxidation of geraniol. It is also present in the oil of lemons. When condensed by potassium bisulphate, III, acetic acid, etc., the double linking is displaced and cymene results. When citral is condensed with acetone it yields Pseudoionone, (CH₃)₂C: CH. CH₂. CH₂C(CH₃): CHCH: CHCOCH₃, boiling at 143-145°. On heating this with dilute sulphuric acid it changes to ionone, an hydroaromatic ketone (B. 27, R. 768).

4. Olefinic Terpenic Acids: Citronellic Acid (Rhodinic Acid?) (B. 29, R. 352), (CH₃)₂C: CH. CH₂. CH₂C(CH₃)H: CH₂. COOH, boiling at 143.5° (10 mm.), is obtained from its nitrile, formed in the dehydration of citronella aldoxime, or by oxidizing

citronellal (B. 29, 905).

Geranic Acid, (CH₃)₂C: CH. CH₂. CH₂C(CH₃): CH. COOH, boiling at 153° (13 mm.), is also obtained from citral. It has also been synthetically prepared from methyl heptenone (see above) and iodacetic ester (B. 29, R. 222). Sulphuric acid converts it into isomeric hydroaromatic isogeranic acid (p. 301).

B. TERPAN OR MENTHAN GROUP.

1. Hydrocarbons. (a) Limonene or Dipentene Group.

The terpenes of this group combine with four atoms of bromine or with two molecules of halogen hydride, but not with N₂O₃. probably are dihydrocymenes. One of the dihydro-p-cymenes has been synthesized (p. 294), but as yet has been too imperfectly studied to compare it with the appended terpenes.

To indicate the constitution of the dihydrocymenes the carbon atoms are provided with numbers:

$$\overset{1}{C} - \overset{2}{C} < \overset{2}{C} - \overset{3}{C} > \overset{4}{C} - \overset{8}{C} < \overset{6}{C}.$$

The dihydrocymene of the formula CH_3 . $CH_4 - CH_2 CH_5 = C(CH_3)_2$, would then be termed Δ_{1,4}(8)-Terpadiëne; and dihydrocymene,

CH₂-CH₂-CH₂-C. CH(CH₃)₂, would be Δ_{1,4}-terpadiëne (B. 27, 436).

Limonene, C₁₀H₁₆, is known in three modifications—d-limonene, 1-limonene, and

[d+1]-limonene or dipentene.
d-Limonene, Citrene, Hesperidene, Carvene, together with pinene, is among the most widely distributed terpenes. It is present in the oil obtained from the shell of Citrus curantium, in citrone oil, in the oil of bergamot, in oil of dill, in oil of celery, etc. It

boils at 175°, $[a]_D = +106.8^\circ$. 1-Limonene occurs in the oil of pine-needles, in oil of fir, and in oil of peppermint. It boils at 175°; $[a]_D = -105^\circ$. **Both limonenes are liquids with an agreeable lemon-like odor.** Their sp. gravity equals 0.846 (20°). They differ from each other, as do their derivatives, almost entirely by their opposite rotatory power (A. 252, 144). The two active limonenes combine with dry bromine to *tetrabromides*, melting at 104°, and having equally large but opposite rotatory power of about $[a]_D = 73^\circ$. Dry hydrochloric acid gas converts them into optically active *limonene hydrochlorides*, while the moist haloid acids change the optically active *limonene hydrochlorides*, while the moist haloid acids change the optically setting limonenes to addition products of $[a]_D = 73^\circ$. active limonenes to addition products of [d+1]-limonene or dipentene. When the optically active limonenes are exposed to elevated temperatures they become dipentenes.

The nitroso-chlorides of the limonenes deserve particular attention (B. 28, 1308; compare also B. 29, 10). d-Limonene forms two chemically identical nitrosochlorides, with, however, different physical properties:

a-d-Limonene-nitroso-chloride melts at 103° ; $[a]_{D} = +313.4^{\circ}$. β -d-Limonene-nitroso-chloride " " 105° ; $[a]_{D} = +204.3^{\circ}$.

d-Carvoxime (p. 320) is formed when these bodies are heated with alcoholic potash. d-Limonene, upon oxidation, yields limonetrite (p. 316).

l-Limonene also forms two differently rotating nitroso-chlorides, which, by loss of hydrochloric acid, rearrange themselves into 1-carvoxime.

[d + 1]-Limonene, Dipentene, Cinene, CH₃. CH₂-CH₂ CH. CH₂ (?) (p. 315) (B. 28, 2145; 29, 4), boils at 175°. It is associated with cineol in Oleum cinæ. It is produced by heating d-limonene, l-limonene, pinene, and camphene to 250-300°; it is, therefore, present in the Russian and Swedish turpentine oil, obtained by application of great heat. It is derived further by the distillation of caoutchouc, and the polymerization of the isoprene, C₅H₈, formed simultaneously (A. 227, 295). It is also produced on mixing equally large quantities of d- and l-limonenes, as well as when pinene is boiled with alcoholic sulphuric acid. It forms, too, on withdrawing water from linalool, terpine hydrate, terpineol, and cineol. It may be prepared pure by heating its hydrochloride with aniline or sodium acetate in glacial acetic acid solution (A. 245, 197; B. 26, R. 319).

Pure dipentene is a liquid with an agreeable lemon-like odor. Its sp. gr. is 0.853, and it is optically inactive.

Although more stable than most of the other terpenes, it can yet be changed into the isomeric terpinene by alcoholic sulphuric acid, or hydrochloric acid. It is oxidized to

p-cymene by concentrated sulphuric acid or phosphorus pentasulphide.

The derivatives of dipentene can be obtained not only from the dipentenes, but also by mixing the corresponding derivatives of dextro- and lævo-limonene.

Dipentene Dihydrochloride, CuH . 2HCl, boils at 1190 (10 mm.) and melts at 500.

The trans-dipentene dihydrobromide, C₁₀H₁₆. 2HBr, from d-limonene, dipentene, terpine, and cineol with hydrobromic acid, melts at 64°.

cis-Dipentene dihydro-bromide, C₁₆H₁₆. 2HBr, melting at 37°, results from the action of HBr upon a well-cooled solution of cineol in glacial acetic acid; see also cisterpine (B. 26, 2864).

Tetrahydro-dipentene Tribromide, Tribromterpan, C10H11Br3, is derived from trans-dipentenedihydrobromide by the action of bromine upon the glacial acetic acid

solution (A. 264, 25).

Dipentene Tetrabromide, C₁₀H₁₆. Br₄, melts at 124° (A. 281, 140).

Dipentene Dihydro-iodide, C₁₀H₁₆. 2HI, melts at 77-79° (A. 239, 13).

Dipentene Nitrosochloride, C₁₀H₁₆(NO)Cl, melts at 102°; see carvoxime, p. 321 (A. 270, 175).

Terpinolene, CH_3 . CH_3 CH_4 CH_5 CH_5 CH_5 CH_5 CH_6 (?), melting at 75° (14 mm.), has

not yet been observed in ethereal oils. It is produced when terpine hydrate, terpineol, and cineol are boiled with dilute sulphuric acid, and by heating pinene with the concentrated acid. Boiling oxalic acid also liberates it from the terpineol melting at 35° (A. 275, 106). The dibromide, C10H16Br2, melts at 70° (B. 27, 447). The tetrabre-

mide, C10 II 16 Br4, is a solid, melting at 116°.

Sylvestrene, $C_{10}H_{16}$, boiling at 176°, occurs in Swedish and Russian turpentine oil. It is optically dextro-rotatory; $[a]_D = +66.32^\circ$ (A. 252, 149). Sulphuric acid imparts an intense blue color to its solutions in anhydrous acetic acid (or in acetic anhydride). Carvestrene and dihydrobenzene show a like behavior (p. 294), while other terpenes under similar conditions exhibit a red to reddish-yellow coloration. It is one of the most stable terpenes. The tetrabromide, C₁₀H₁₆Br, melts at 135°. The dihydrockloride, C10 H1xCl2, melts at 72°, the dihydrobromide at 72°, and the dihydroiodide at 67°. The

Carvestrene, $C_{10}H_{16}(NO)CI$, melts at 107° (A. 252, 150).

Carvestrene, $C_{10}H_{16}(NO)CI$, melts at 107° (A. 252, 150).

Carvestrene, $C_{10}H_{16}$, boiling at 178°, results from the distillation of carylamine hydrochloride. It is probably the optically inactive isomeride corresponding to sylvestrene (B. 27, 3485). Blue coloration, see sylvestrene. The dihydrochloride melts at 52°, and

the dihydrobromide at 48-50°.

Thujen, Tanactene, $C_{10}|I_{16}$, from thujonamine hydrochloride, boils at 172-175° (760 mm.), 60-63° (14 mm.); sp. gr. 0.840, $n_D = +1.476$ (20°) (A. 286, 99).

(b) Terpinenes and Phellandrene, C₁₀II₁₆.—Both are distinguished from the terpenes of the limonene or dipentene groups by the fact that they do not yield tangible derivatives either with bromine or the haloid acids. However, they do form nitrosites

with N2O3.

Terpinene, C₁₀II₁₆, boiling at 179-181°, occurs in cardamom oil. It results on boiling dipentene, terpine, phellandrene, cincol, terpineol, or dihydrocarveol with dilute alcoholic sulphuric acid, and when pinene is shaken with a little concentrated sulphuric acid. It is characterized by its stability toward dilute mineral acids. Its production together with dipentene, when formic acid acts upon linalool, is very noteworthy. It is the most stable of all the terpenes, and is not changed into any other terpene (A. 239, 38). Terpinene is optically inactive; it has an odor like that of cymene. Nitrous acid converts it into Terpinene Nitrosite, C₁₀H₁₆(NO)O. NO or C₁₀H₁₅(N.OH). O. NO, melting at 155°, and yielding nitrolamines with bases. Ammonia converts it into terpinene nitrolamine, C₁₀H₁₅(N.OH). NH₂, melting at 118° (A. 241, 320). Phellandrene, C₁₀H₁₆, is known in two optically active forms. Both boil at 170°, and have not yet been obtained in a pure condition. They may be classed with the not unstable terpence. A Phellandring Nitrous

most unstable terpenes. d. Phellandrene occurs in the oil of water fennel, Phellandrium aquaticum, etc. (A. 246, 233). l-Phellandrene is found in Australian eucalyptus oil

from Eucalyptus amygdalina, etc.

d-Phellandrene Nitrosite and l-Phellandrene Nitrosite, $C_{10}II_{10}(NO)O$. No. melt at 105°. The d-nitrosite is keyorotatory, $[a]_D = -183.20^\circ$, while the l-nitrosite is dextro-rotatory. Metallic sodium and alcohol reduce these nitrosites to ketones, C10H18O, which have proved to be d. and l-tetrahydrocarbons, inasmuch as they form by their union a racemic tetrahydrocarvone identical with the one prepared in another manner (p. 318) (A. 287, 371).

(c) Hydroterpenes.—Hydrocarbons derived from menthol and tetrahydrocarveol as starting-out substances, and containing two to four atoms more of hydrogen than the preceding bodies, bear close kinship to the latter. The two alcohols just mentioned are derived in such a manner from hexahydro-p-cymene that in both of them there are present secondary ring-alcohols of this hydrocarbon. When they lose water, menthene and carvomenthene are produced. By reducing menthol with HI, or menthyl chloride with sodium and alcohol (B. 29, 317), a hydrocarbon was obtained, which probably is—

Hexahydrocymene, Menthonaphthene, CH₃>CH . CH < CH₂. CH₂ > CH . CH₃ > CH . CH₄ CH₁ CH₂ CH . CH₄, boiling at 169°. Its specific gravity equals 0.8066 (0°). The hexahydrocymene obtained in the reduction of terpine hydrate (B. 23, R. 433) and from resin oil is identical with this hydrocarbon.

Tetrahydro-p-cymenes are the two hydrocarbons-

Carvomenthene, $C_{10}H_{18}$, boiling at 175°, and Menthene, Menthomenthene, $C_{10}H_{18}$, boiling at 167°, with sp. gr. 0.806 (20°) or 0.814 (20°). The latter is best made by acting with potassium phenolate upon menthyl chloride (B. 29, 1843). See B. 29, 11, for the mitroso-chlorides.

The constitution of the two hydrocarbons follows from their relation to carvacrol and menthol. Carvacrol (p. 145) readily results from a rearrangement of carvone (constitution, compare p. 320), which upon reduction yields tetrahydrocarveol (p. 314), with which menthol is isomeric. The constitution of menthol, on the other hand, is proved by conversion of the corresponding ketone, menthone (p. 318), into 3-chlorcymene and thymol. By removing water from these alcohols, or hydrogen chloride from their chlorides, two different tetrahydrocymenes were formed:

$$\begin{array}{c} \text{CH}_{3}\text{-}\text{CII} & \xrightarrow{\text{CH}_{2}}\text{-}\text{CII}(\text{OH}) \\ \text{CII}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{2}}\text{-}\text{CH} \\ \text{CH}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{2}}\text{-}\text{CH} \\ \text{CH}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CO}}\text{-}\text{CH} \\ \text{CH}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CO}}\text{-}\text{CH} \\ \text{CH}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CO}}\text{-}\text{CH} \\ \text{CH}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CH} \\ \text{CH}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} \\ \text{CH}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} \\ \text{CH}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} \\ \text{CH}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} \\ \text{CH}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} \\ \text{CH}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} \\ \text{CH}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CH}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} \\ \text{CH}_{3} & \xrightarrow{\text{CH}_{3}}\text{-}\text{CII} \\ \text{CH}_{3} &$$

When oxidized with potassium permanganate menthene yields (1) menthene glycol (p. 315), (2) a keto-alcohol boiling at 105° (13.5 mm.), and (3) the fatty acids arising from menthone (B. 27, 1636).

2. ALCOHOLS OF THE TERPAN OR MENTHAN GROUP.

I (a) Monacid Menthan Alcohols.—Hexahydro-p-cymene yields the isomeric menthols.

Secondary Menthols.—l-Menthol, Mentha Camphor, Oxyhexahydro-cymene, 5-Methyl-2 isopropylhexahydrophenol,

CH₂. CH₂. CH₁(OH₂) CH . CH(CH₃)₂ (see above), melting at 42° and boiling at 212°. It is the chief constituent of peppermint oil (from *Mentha piperita*). It is formed in the reduction of menthone (J. pr. Ch. [2], 55, 14) and is oxidized by chromic acid to 1-menthone (p. 318). By the exit of water it yields menthene (see above), and by reduction hexahydrocymene results (above). Potassium permanganate converts it into

oxomenthylic acid, CH₁. CH₂. CO₂H

CH₃. CH₄. CH₄. CH₄. CO₂H

(15 mm.) (A. 289, 362), and β-pimelic acid or β-methyl adipic acid,

CH₃. CH₄. CO₂H

CH₄. CO₄H

CH₄. CH₄. CO₄H

CH₅. CH₄. CH₄. CO₄H

CH₄. CH₄. CH₄. CO₄H

CH₄. CH₄. CH₄. CH₄. CO₄H

CH₄. CH₄. CH₄. CH₄. CO₄H

CH₅. CH₆. CH of ester formation would indicate menthol to be a secondary alcohol.

Menthyl Chloride, C₁₀H₁₉Cl, boils at 204°. The ethyl ether boils at 212°, and the benzoyl ester melts at 54°.

Tetrahydrocarveol, CH₃. CII < CH(OH) — CH₂ > CH . CH(CH₃)₂, isomeric with menthol, is a thick oil, volatile without decomposition. It is formed when tetrahydrocarvone and carvenone (p. 319) are reduced in moist ethereal solution with metallic sodium. Its genetic connection with carvacrol (see above) would indicate its constitution.

Thujamenthol, Bihydroisothujol, C₁₀H₁₉. OH, boiling at 211-212°, with sp. gr. 0.9015, n_D = 1.4636 (20°) (B. 28, 1958), results from the reduction of isothujone. Although carvenone and isothujone both yield carvacrol with ferric chloride, they yet form different hexabydromonoxycymenes, in which the OH-group should occupy the

Tertiary menthols are produced when their hydriodic acid esters, addition products of III and menthene by means of carvomenthene, are treated with silver acetate, and the

resulting acetates then saponified (see also B. 29, 1844).

Tertiary Menthol, CH₃. CH CH₂ CH₂ CH₃ C(OH). CH(CH₃)₂, boiling at 100° (20 mm.), has a faint peppermint-like odor.

Tertiary Carvomenthol, CH₃C(OII) < CH₂ - CH₃ - CH₄ > CH . CH(CH₃)₂, boils at 96-100° (17 mm.).

(b) Diacid Alcohols.—In this group are the two terpines, cis-terpine and trans-terpine, corresponding to the cis- and trans-dipentenedihydrobromides, with which they are intimately related. At present the following formulas are assigned them (see B. 29, 5):

These are in harmony with the oxidation of terpine hydrate to terebic acid (p. 324), as well as with its formation from linalool (p. 310). Cineol is to be regarded as the oxide corresponding to the cis-terpine.

Terpine, cis. Terpine, $C_{10}II_{18}(OH)_2$, melting at 104° and boiling at 258°, readily parts with water and becomes terpine hydrate, $C_{10}H_{18}(OH)_2 + H_1O$, melting at 117°, from which it is prepared by protracted heating to 100°. Terpine corresponds to cisdipentenedihydrobromide (p. 311), from which it can be obtained by treatment with silver acetate in glacial acetic acid, and saponifying the resulting diacetyl derivative with alco-holic potash. Terpine hydrate is also produced if turpentine oil is allowed to stand with dilute nitric acid and alcohol (A. 227, 284), as well as from pinene (p. 322), dipentene, and d-limonene with dilute acids. It forms, furthermore, on bringing dipentene and d-limonene dihydrochloride in contact with water, and when terpineol (p. 316) and cineol are acted upon with dilute acids.

The haloid acids convert terpine hydrate into the cis- and trans-dihydrohalides of When boiled with dilute acids it passes into terpineols (B. 27, 443, 815), cineol, dipentene, terpines, and terpinolenes.

trans-Terpine, C₁₀H₁₈(OII)₂, melting at 156-158° and boiling at 263-265°, is formed

from trans-dipentenedihydrobromide (see cis-terpine), into which it finally reverts upon

treatment with hydrogen bromide. It does not combine with water of crystallization.

Cineol, C₁₀H₁₈O, boiling at 176°, with sp. gr. 0.923 (16°), n_D = 1.4559, is a liquid with a camphor-like odor. It occurs in many ethereal oils, in Oleum cine, the wormseed oil of Artemisia cina, cajeput oil, eucalyptus oil, rosemary oil, etc. Hydrochloric acid gas conducted into a petroleum ether solution of cineol precipitates an unstable addition product, C₁₀H₁₈O. HCl (?), which water resolves into its components, and which serves for the separation of cineol. In glacial acetic acid solution the haloid acids change cincol into dipentene dihydro-halides. At low temperatures hydrogen bromide produces cis-dipentenedihydrobromide (p. 312). P₂S₅ converts cincol into cymene. Potassium permanganate oxidizes cincol (1) into cincolic acid (2), the anhydride (3) of which yields, upon distillation, methylhexylene ketone or methyl heptenone (4) (constitution, p. 310), while the latter may be arranged to m-dihydroisoxylene (5) (p. 294). This series of reactions is shown in the following diagram:

$$(1) CH_{3} \longrightarrow CH \qquad (2) CH_{3} \longrightarrow CH \qquad (3) CH_{3} \longrightarrow CH \qquad (CH_{3})_{2} \stackrel{\cdot}{C} \qquad CO_{2}H \qquad (CH_{3})_{3} \stackrel{\cdot}{C} \qquad CO \qquad (CH_{3})_{3} \stackrel{\cdot}{C} \qquad CO \qquad (CH_{3})_{4} \stackrel{\cdot}{C} \qquad CO \qquad (CH_{3})_{5} \stackrel{\cdot}{C} \qquad (CH$$

Cineolic Acid melts at 196-197° with decomposition; its anhydride melts at 78°

and boils at 157° (13 mm.).

Menthene Glycol, C₁₀II₁₈(OH)₂, melting at 77° and boiling at 130° (13 mm.), results when menthene is oxidized with potassium permanganate (B. 27, 1636).

(c) Triacid Menthan Alcohols have been obtained by oxidizing menthene alco-

hols with potassium permanganate.

1. Trioxyhexahydrocymene, $C_{10}H_{11}[2,8,9](OH)_3$ (1), from dihydrocarveol (see below), is a syrup, and with dilute sulphuric acid yields an indifferent oxide, $C_{10}H_{16}(\cdot)$, boiling at 196–199° (A. 277, 152), while upon oxidation with chromic acid it forms a ketone-alcohol: 5-acetylhexahydro-o-cresol, melting at 58° (2), which upon further oxidation changes to hexahydro-m-oxy-p-toluic acid, melting at 153° (3). The constitution of this last acid is evident from its conversion by bromine into m-oxy-p-toluic acid, melting at 203° (4). These experiments give rise to the constitution formulas (B. 28, 2141):

2. Trioxyhexahydrocymene, Dioxyterpineol, C₁₀H₁₇(OH)₃, melting at 121°, formed from the terpineol melting at 35°, passes into carvenone (p. 319) when it is acted upon with delute sulphuric acid (A. 277, 122).

3. Trioxyhexahydrocymene, $C_{10}H_{17}[1,4,8](OH)_s+3H_sO$, melts in the anhydrous state at 110–112° and boils at 200° (20 mm.). It is formed from $\Delta_{4/8}$ terpineol

(B. 28, 2296).

(d) Tetracid Menthan Alcohols.—When d-limonene is oxidized it yields Limonetrite, C₁₀H₁₈(OH)₄, melting at 192° (B. 23, 2315). This is a sweet-tasting body belonging to this class of compounds. Its constitution is variously considered, depending upon the views held in regard to the point of double union in limonene (B. 28, 2140).

11. Menthene Alcohols, C₁₀H₁₇OH, when oxidized with potassium permanganate,

yield triacid alcohols.

The reduction of the ketones, carvone, eucarvone (p. 321), and thujone (p. 319), or tanacctone, gives rise to three different alcohols: $C_{10}H_{17}$. OH: (1) Dihydrocarveol, boiling at 224° (760 mm.), 112° (14 mm.), with sp. gr. 0.927 (27°) $n_D = 1.48168$, is optically active, and has an agreeable odor, recalling that of the terpineols; (2) Dihydroeucarveol boils at 109° (21 mm.); (3) Thujyl Alcohol, Tanacctyl Alcohol, boils at 92.5° (13 mm.). Its sp. gr. equals 0.9249, with $n_D = 1.4635$.

Terpineols: Terpineol, CH₂.

35°, is formed from terpine hydrate (p. 314) by the withdrawal of two molecules of water (A. 275, 104). It combines very readily with nitrosyl chloride. When hydrogen chloride is withdrawn from this body an oxyoxime, melting at 134°, is produced. Boiling dilute acids change it to carvacrol and carvone (B. 29, R. 587). Hence it follows that in terpineol and carvone the carbon atoms are similarly grouped. Terpineol nitrosochloride and limonene nitrosochloride are correspondingly constituted (p. 311) (B. 29, 9). Potassium permanganate oxidizes terpineol (1) into trioxyhexahydrocymene, melting at 121° (2), while with chromic acid it yields a ketone-lactone, homoterpenylic acid methyl ketone, C₁₀ II₁₆O₃ (3), which, under the influence of potassium permanganate, breaks down into acetic acid and terpenylic acid (4) (p. 324). Therefore, in terpineol melting at 35°, the OII-group probably is in union with carbon atom 8 (B. 28, 1773, 1779):

When terpineol is heated with potassium bisulphate it changes to dipentene, and when boiled with oxalic acid to terpinolene (p. 312) (A. 275, 104).

The same constitution has been recently assigned to an optically active terpineol boiling at 215°, which has been made from d-limonene hydrochloride; it has the odor both

of the mayflower and of lilac (B. 28, 2189). Terpineol, $CH_3C(OH) < CH_2 - CH_2 > C = C(CH_3)_2$, melts at 69°. Its acetate results on treating tribromterpan or tetrahydrodipentene tribromide (p. 311) with glacial acetic acid and zinc-dust. HBr converts it into dipentene dihydrobromide, and with NOCI a blue nitrosochloride, just as tetramethylethylene does. Consequently it probably also contains a tertiary-tertiary double union. In addition, its OH-group must be in such a position that dipentenedihydrobromide can be produced with hydrogen bromide. III. Menthadiëne Alcohols.—Carveol Methyl Ether, C₁₀II₁₆OCH₃, boiling at

208-212°, with sp gr. 0.9065, $n_D = 1.47586$ (18°), represents the methyl ether of such an alcohol. It is formed in the action of sodium upon the alcoholic solution of limonene tetrabromide. Chromic acid oxidizes it to inactive carvone (A. 281, 140). Isocarveol, C₁₀H₁₅OH, is obtained from pinylamine (A. 279, 387).

3. BASES OF THE TERPAN OR MENTHAN GROUP.

Menthan bases have been obtained by the reduction of the oximes of the menthan ketones with sodium and alcohol, or upon heating the ketones with ammonium carbonate.

R-Menthylamine and L-Menthylamine,

CH₃. CH < CH₂ - CH₃ - CH₃ CH . CH(CH₈)₂, boiling at 205°, have an unpleasant odor and attract CO, from the air. The bases have opposite, but unequal, rotatory power; the same is true of their derivatives (A. 276, 299). They can be separated by means of their formyl compounds, both of which are formed on heating menthene with ammonium formate. R. Formylmenthylamine, melting at 117°, dissolves with more difficulty. L. Formylmenthylamine melts at 102°. L-menthylamine can also be obtained from 1-men-

Tetrahydrocarvylamine, Carvomenthylamine,

Tert. Menthylamine, CH₃. CH
$$<$$
CH₂ $-$ CH₂ $-$ CH₂ $>$ C(NH₃)CH(CH₃)₂, and Tert. Carvomenthylamine, CH₃(NH₃)C $<$ CH₂ $-$ CH₂ $-$ CH₂ $-$ CH . CH(CH₃)₂, have been obtained

by the interaction of menthene hydrobromide, carvomenthene hydrobromide, and silver cyanate, with subsequent saponification (B. 26, 2270, 2562).

Menthene bases have been prepared by the reduction of the oximes of menthene ketones.

Dihydrocarvylamine, $C_{10}H_{17}NH_{1}$, boiling at 219°, with sp. gr. 0.889 (20°), $n_D=1.48294$, is optically active, and is obtained from carvonoxime, $C_{10}H_{14}$: NOH. Its hydrochloride breaks down completely at 200° into ammonium chloride and terpinene, which in so doing passes partly into cymene (A. 275, 120; B. 24, 3984). Carylamine, C. H., NH, from caronoxime, is stable in the presence of potassium permanganate, but is rearranged by hydrochloric acid into isomeric vestrylamine, the hydrochloride of which yields carvestrene upon the application of heat. Dihydroeucarvylamine, C₁₀H₁₇, NH₂, is formed from encarvoxime (B. 27, 3487). a-Thujonamine, $C_{10}H_{11}NH_{11}$, is obtained from the thujone oxime melting at 52°. Its hydrochloride, when heated, yields thujene or tanacetene (p. 312). The thujonoxime, melting at 90°, yields an isomeric β -thujonamine. A third isothujonamine results from isothujonoxime (A. 286, 96), melting

at 119°. Pulegonamine (A. 262, 13; B. 29, R. 173).

Nitrolamines have been obtained from nitroso-chlorides—e.g., limonene—by trans-

position with primary and secondary bases.

4. THE RING-KETONES OF THE TERPAN OR MENTHAN GROUP.

Ketones like these are found in the vegetable kingdom. They are produced by the oxidation of the corresponding secondary alcohols, and by continued oxidation they change to cyclic and aliphatic carboxylic acids,—decomposition products,—the constitution of which furnish insight into the constitution of the ring-ketones and their derivatives. The ring-ketones of the terpan-group, like other ketones, are characterized by their oximes and the sparing solubility of their semicarbazones.

(a) Ketomenthans, Ketohexahydro-p-cymene, C₁₀H₁₈O.

Menthone, CH_3 . $CH < \stackrel{CH_2}{CH_1}$. CO > CH. $CH(CH_3)_3$, boiling at 206°, sustains the same relation to menthol that camphor bears to borneol (p. 324). It occurs in American and Russian peppermint oils, together with menthol, esters of menthol, menthene, and limonene. Menthone is known in two optically active modifications. 1-Menthone is obtained upon oxidizing menthol with potassium bichromate and sulphuric acid at a temperature not exceeding 50° (A. 250, 322). Its sp. gravity equals 0.896 (20°), $[a]_p = -28°$. Concentrated sulphuric acid, in the cold, rearranges 1-menthone to d-menthone, $[a]_p = +28°$.

The constitution of menthone (see p. 313) is demonstrated (1) by its conversion into 3-chlorcymene; PCl_5 changes menthone to dichlorhexahydrocymene, which splits off hydrogen chloride and becomes tetrahydrochlorcymene: this in turn, by the action of bromine and quinoline, loses hydrogen and 3-chlorcymene results (B. 29, 314). (2) By the formation of thymol (p. 144) through the elimination of 2HBr from Dibrom-menthone, $C_{10}II_{16}Ir_5O$, melting at 80°, which is produced in the bromination of menthone in chloroform solution (B. 29, 418).

When 1-menthone is reduced by sodium it forms 1-menthol, while with ammonium formate the product is L-menthylamine (p. 317). Potassium permanganate oxidizes it to oxomenthylic acid, CH₂, CH₂, CO₂H CO. CH(CH₃), and β-methyl adipic acid (1, 454; B. 27, 1820). Amylnitrite and hydrochloric acid convert menthone into nitrosomenthone and menthoximic acid, melting at 98°. This is the oxime of oxomenthylic acid (B. 29, 27). Sodium and amyl formate change menthone to oxymethylene menthone, boiling at 121° (12 mm.). See B. 29, 1599, for the condensation of menthone with aldehydes.

1-Menthoxime melts at 59° and boils at 250°; $[a]_D = -42°$. When it is treated with PCl₅ in chloroform, or with acetic anhydride, or concentrated sulphuric acid, it becomes iso-1-menthoxime, melting at 119° and boiling at 295°; $[a]_D = -52.25°$. P₁O₅ converts both oximes into menthonitrile, C₂H₁₇CN, boiling at 225°, which boiling sodium alcoholate changes to menthoamide, C₂H₁₇CO . NH₂, melting at 105°, and liquid menthoic acid, C₂H₁₇. CO₂H.

Tetrahydrocarvone, CH₃. CH. < CO . CH₂ CH. CH(CH₃)₂ (constitution, see carvomenthene, p. 313), with sp. gr. 0.904 (20°), n_D = 1.45539, is produced in the oxidation of tetrahydrocarveol (p. 314). The axime melts at 104°, the a-isoxime at 51°. β-Isoxime melts at 104°, the a-isoxime at 51°. β-Isoxime melts at 104°. (A. 277, 133; 286, 107; B. 26, 822). When oxidized with potassium permanganate or treated with amyl nitrite and hydrochloric acid, tetrahydrocarvone is decomposed like menthone with the production of an acid, CH₃. CO . CH. — CH. CH. C₃H₁, β-isopropyl-δ-acetyl valeric acid,

isomeric with oxomenthylic acid. Energetic oxidation produces isopropyl succinic acid (B 29, 27).

Thujamenthone, boiling at 208°, with sp. gr. 0.891, $n_D = 1.44708$ (20°), results from the oxidation of thujamenthol (B. 28, 1959).

(b) Ketomenthenes, $C_{10}H_{16}O$, occur to a certain extent in nature, others are produced by the oxidation of the corresponding alcohols. They contain one double union.

CH₂

CH₂

CH₂

CH₂

CH₂

CH₂

CH₂

CH₃

CH₂

CH₂

CH₃

CH₂

CH₃

CH₂

CH₃

CH₄

CH₂

CH₂

CH₃

CH₄

CH₂

CH₃

CH₄

CH₂

CH₄

CH₄

CH₅

CH₅

CH₅

CH₅

CH₆

CH₇

CH₇

CH₇

CH₈

CH₈

CH₈

CH₉

with sp. gr. 0.928 (19°), $n_D = 1.47174$, are obtained from the corresponding dihydrocarveols. The oximes melt at 88°, and unite to the inactive [d+1]-oxime, melting at 115°. Boiling ferric chloride converts dihydrocarvone into carvacrol—compare carvenone

and carone. Oxidation with potassium permanganate and afterward with chromic acid changes it to 2,5-methyl acetyl cyclohexanone (p. 316 and B. 28, 2147, 2704).

Carvenone, Carveol, boiling at 232°, with sp. gr. 0.927, n_D = 1.4822, is produced together with cymene when dioxyterpineol, melting at 121°, is digested with dilute sulphuric acid; also from dihydrocarvone with sulphuric acid (A. 286, 129). Its oxime melts at 91°, the semicarbazone at 202°. It resembles isothujone very much (B. 28, 1955).

Dihydroeucarvone, boiling at 87° (14 mm.), is obtained from dihydroeucarveol (p. 316) (B. 28, 646). The following ketones, carone and thujone, isomeric with the ketomenthenes, show the behavior of saturated ketones; hence it is assumed that double rings

are present in them as in camphene and pinene.

Carone boils at 210°, being at the same time rearranged into carvenone. It results on treating dihydrocarvone hydrobromide with alcoholic potash. It reverts to dihydrocarvone hydrobromide again through the action of hydrobromic acid; whereas sulphuric acid changes it to oxytetrahydrocarvone. Carone is relatively stable toward potassium permanganate, which first attacks it at the water-bath temperature, forming caronic acid, C, H₁₀O₁, cis- melting at 175° (the *anhydride* melting at 55°), and trans- melting at 212°. We thus have a cis- and trans- modification of the acid, which would prove caronic acid to be an analogue of the trimethylenedicarboxylic acids. It is very probably dimethyl trimethylene-1,2-dicarboxylic acid; then in carone there would be a combined tri- and hexamethylene ring. Caronic acid is very stable; hydrobromic acid alone decomposes it readily and converts it into the isomeric terebic acid (p. 324) (B. 29, 2796):

Thujone, Tanacetone, (CH₃)₃. CH. CH. CH. CO CH₂. CH—CH. CH₃ (?) (compare the cam-

phor formulas, p. 328), boiling at 200°, with sp. gr. 0.917 and $n_D = 1.4511$, occurs in the oil from Tanacetum vulgare, in that of worm-wood, in thuja-oil, oil of absinthe, and in that of Artemisia Barellieri. Potassium permanganate oxidizes thujone to a- and β -thujaketone carboxylic acids, melting at 74° and 78°. Upon the application of heat the a-acid is changed to the β -form, which probably has the constitution CH_1 . $CO.CH_2$. CH_2 . CH_3 . CH_4 . $CO.CH_3$. CH_4 . $CO.CH_3$. CH_4 . $CO.CH_3$. CH_4 . $CO.CH_4$. CO.pare upon this point, as well as in regard to the constitution of thujone, isothujone and carvotanacetone (B. 30, 423, 429; 29, 885). Alcoholic sulphuric acid converts thujone into isothujone. When heated to 280° it is converted into carvotanacetone (B. 28, 1959). Its oxime, melting at 54°, is changed to carvacrylamine (B. 30, 325) by alcoholic sulphuric acid.

Isothujone boils at 231°; sp. gr. 0.927, with $n_D=1.4822$. Formation—see thujone. Its oxime melts at 119°. The a- and β -semicarbazones melt at 208° and 148°

(B. 28, 1955).

Carvotanacetone boils at 228°; sp. gr. 0.932 (21°), with $n_D = 1.47926$. Formation—see thujone. Its oxime melts at 119°. The semicarbazone melts at 177° (B. **28**, 1959).

Pulegone, CH_1 , $CH < {CH_1 \cdot CO \atop CH_2 \cdot CH_2} > C = C(CH_1)_2$, boils at 221°; sp. gr. 0.936, with $n_D=1.4846$. It is present in the ethereal oils from Mentha pulegium and Hedeona pulegeides, which occur in commerce under the name polei-oils. The addition of hydrogen to pulegone produces menthene. B. Methyl adipic acid and acetone are produced by its oxidation, while it splits, upon heating with anhydrous formic acid, into acetone and 3-methyl hexanone, which is also oxidized to β -methyl adipic acid (A. 289, 337):

$$\begin{array}{c} CH_{3}.CH < \stackrel{CH_{2}.CO}{CH_{2}.CH_{3}} > C = C(CH_{3})_{3} \xrightarrow{2H} CH_{2}.CH < \stackrel{CH_{2}.CO}{CH_{2}.CH_{3}} > CH.CH(CH_{3})_{3} \\ & \\ CH_{3}.CH < \stackrel{CH_{3}.CH}{CH_{2}.CH_{3}} > CH_{2}(+ CO(CH_{3})_{3}) \longrightarrow CH_{3}.CH < \stackrel{CH_{3}.COOH}{CH_{3}.CH_{3}} COOH. \end{array}$$

When citronellal is condensed with acetic anhydride it yields a secondary cyclic alcohol-isopulegone-which is very similar to pulegone, and by hydrolytic decomposition yields 3 methyl cyclohexanone (B. 30, 22). Isopulegone is reconverted into pulegone by long shaking with a baryta solution.

(c) Menthadiën Ketones, Ketodihydro-p-cymenes, C,H14O.—The most important member of this group is carvone, formerly called carvol. Its importance is due to its intimate relationship to carvacrol and limonene, which are isomeric with it. Carvone is known in three modifications, the d-, 1-, and [d + 1]-.

d-Carvone, CH_3 . C CH_4 C. $CH(CH_3)_2$ (B. 28, 31), or CH_4 . CH_5 CH_5 CH_5 CH_5 CH_5 CH_6 CH_6 CH_6 CH_7 CH_7 CH_8 CH_7 CH_8 CH_8 CH_8 CH_8 CH_8 CH_8 CH_9 CH_9 (B. 28, 2145), $[a]_D = +62^\circ$, boiling at 225°, occurs in oil of cumin and in dill-oil. When heated with potassium hydroxide or phosphoric acid it changes to isomeric carvacrol or 2-methyl-5-isopropyl-oxybenzene; hence it is assumed that in carvone the CO-group, like the OH-group in carvacrol, is in the ortho-position with reference to the methyl group. Reduction changes it to dihydrocarveol (p. 316), while ammonium formate converts it into dihydrocarvylamine (p. 317). Potassium permanganate oxidizes carvone to oxyterpenylic acid, C₈H₁₂O₅, which easily changes to a dilactone, C₈H₁₀O₄, melting at 129° (B. 27, 3333; 28, 2148). The carvones combine with hydrogen sulphide, hydrogen chloride, hydrogen bromide, and bromine (B. 28, R. 548).

1-Carvone, $[a]_D = -62^\circ$, boiling at 225°, occurs in curomoji oil (B 24, 81). It is obtained pure by distilling its hydrogen sulphide com-

pound, melting at 187°, with caustic potash.

[d+1]-Carvone, boiling at 225°, is formed on mixing d- and 1-carvone, as well as by oxidizing carveol methyl ether (p. 317). Formation

from terpineol, B. 29, R. 587.

The three carvones are linked through the three carvoximes to the three corresponding limonenes. The carvoximes are prepared not only by the action of hydroxylamine upon the carvones, but also upon boiling the limonene nitrosochlorides with alcoholic potash. d-Carvone and 1-limonene correspond on the one side to each other, while on the other 1-carvone and d-limonene correspond, inasmuch as 1-limonene nitrosochloride yields d-carvoxime, and d-limonene nitrosochloride l-carvoxime.

d-Carvoxime, $[a]_D = +39.71^\circ$, and l-Carvoxime, $[a]_D = -39.34^\circ$, melt at 72°. [d+1]-Carvoxime melts at 33° and is obtained from dipentene nitrosochloride (p. 312). Concentrated sulphuric acid rearranges carvoxime to p-amidothymol (compare

Bucarvone, C₁₀H₁₄O, boiling at 104° (25 mm.), with sp. gr. 0.948 (20°), results on treating carvone hydrobromide with alcoholic potash, and with methyl alcoholic potash at a definite temperature forms a deep-blue, unstable color. The oxime melts at 106°. The semicarbatone, C₁₀H₁₄: N. NH. CO. NH, melts at 184°. The reduction of eucar-vone produces dihydroeucarveol (p. 316); see B. 29, 18, for its oxidation.

Isocarvone, C₁₀H₁₄O, boiling at 222-224°, with sp. gr. 0.989 (19°), n_D = 1.5067, results from the oxidation of isocarveol (p. 317). Its oxime melts at 98°.

C. CAMPHAN GROUP.

Camphor is the most important derivative of this group. Bredt considers it to be the ketone of a hexahydrobenzene in which two carbon atoms, occupying the p-position, are linked to each other by the group CH₂. C. CH₃. To one of these carbon atoms there is also attached a methyl group. It would, therefore, be necessary to assume that in the hydrocarbons closely allied to camphor there was probably a similar car**bon** skeleton present:

$$\begin{array}{c|ccccc} CH_3-CH-CH_2 & CH_3-CH-CH & CH_3-CH-CH_2 \\ |CH_3.c.CH_3| & |CH_3.c.CH_3| & |CH_2-CH-CH \\ |CH_3-c.CH_3| & |CH_3-CH-CH \\ |CH_3-CH_3| & |CH_3-CH-CH \\ |CAmphor,C_{10}H_{10}O & |CAmphene \\ |CAmphene & |CH_3-CH-CH| \\ |CH_3-CH| \\ |CH$$

Fenchone is very much like camphor. Hence, fenchene, derived from fenchone, will be classed with camphene and pinene.

I. HYDROCARBONS.

Camphene, C₁₀H₁₆ (Constitution, see above), melting at 48° (53°) and boiling at 160°, $n_D = 1.45514$ (54°), is the only known solid terpene. It is known in a d-, l-, and an optically inactive modification; these are similar in chemical deportment. Camphene has been found, by a rearrangement, in isoborneol, in the oil from Andropogon nardus, and in camphor oil (B. 27, R. 163). It is obtained (1) from borneol by the action of potassium bisulphate at 200°; (2) by the action of ZnCl, or dilute sulphuric acid upon isoborneol; (3) when sodium acetate and glacial acetic acid at 200° act upon pinene hydrochloride; and (4) on digesting bornyl chloride (p. 325) with aniline.

Camphene Hydrochloride, $C_{10}H_{11}Cl$, melting at 149-151°, is produced when HCl is conducted into an alcoholic camphene solution. It is identical with the isobornyl

chloride obtained from isohorneol (p. 325).

Camphene Dibromide, C₁₀H₁₆Br₁, melting at 89°, together with liquid bromcamphene, C₁₀H₁₈Br (B. 29, 544, 697, 900), is formed when bromine in petroleum ether acts upon camphene.

Camphene, treated with glacial acetic acid and concentrated sulphuric acid, yields isoborneol acetate.

Chromyl chloride in carbon bisulphide solution changes camphene to the compound Chromyl chloride in carbon obsulptime solution changes camplaine to the camplaine. C₁₀H₁₆. 2CrO₂Cl₂. Water decomposes this body, with the formation of an aldehyde—camphenilan aldehyde, C₁₀H₁₆O, melting at 70° and boiling at 96° (14 mm.). The oxidation of this aldehyde gives rise to two isomeric camphenilanic acids, C₁₀H₁₆O, melting at 65° and 118°, which can be changed through the corresponding a-brom-acid into axycamphenilanic acid, camphenilol acid, C₁₀H₁₆O₃, melting at 171°. This latter acid is also formed when camphene is oxidized with potassium permanganate. Its cutter oxidation causes the elimination of carbon dioxide and the formation of a ketone further oxidation causes the elimination of carbon dioxide and the formation of a ketone, Camphenilon, C₁₀II₁₄O, melting at 35° and boiling at 81° (12 mm.). This is the lower ring homologue of camphor (p. 326); it resembles the latter in odor and in chemical behavior. The camphenilan aldehyde and camphenilol-acid very probably owe their production to a camphene glycol (p. 325) and camphorquinone, formed at the first, but which sustain rearrangements like those of pinacone and benzilic acid. This change is represented in the following formulas (privately communicated by J. Bredt and Jagelki; compare C., 1897; 1, 1056):

Dilute nitric acid converts camphene into tribasic Carboxyl-apocamphoric Acid, Campho-acid, C₁H₁₁(CO₂H)₃, melting at 196°; when heated this becomes dibasic apocamphoric acid (p. 322). Chromic acid oxidizes camphene to camphor.

Dihydrocamphene, C₁₀H₁₈, melting at 155° and boiling at 159°, is formed when sodium and alcohol act upon l-pinene hydrochloride and d-bornyl chloride. It is opti-

cally inactive, and sublimes with ease (v. Rosenberg, private communication).

Pinene, C₁₀H₁₆ (see above for constitution), boiling at 155°, with sp. gr. 0.858 (20°), $n_D = 1.46553$ (21°), is the chief ingredient of the turpentine oils obtained from the different varieties of pine. It also occurs in many other ethereal oils—eucalyptus, juniper-berry, sage, etc.

Turpentine Oil.—Turpentine, the resinous juice exuding from various Conifera, consists of a solution of resins in turpentine oil which distils with steam, while the resin (colophony) remains behind. Turpentine oil is a colorless liquid, boiling at 158-160°, with sp. gr. equaling 0.856-0.87. Its peculiar odor is due to the aldehyde-like oxidation products (B. 29, R. 871) produced by the action of sunlight.

It is almost insoluble in water, but is miscible with absolute alcohol and ether. dissolves sulphur, phosphorus, and caoutchouc, and serves for the preparation of varnishes

and oil-colors.

The turpentine oils, according to their origin, are distinguished by different rotatory

When turpentine is conducted through tubes heated to redness, isoprene (p. 309), toluene, m-xylene, naphthalene, anthracene, methyl anthracene, phenanthrene, etc., are produced. Heated with iodine, turpentine oil yields m-xylene, little p-xylene and cymene, pseudocumene, mesitylene, durene, and polyterpenes.

d Pinene is obtained by the fractional distillation of American oil of turpentine, and 1-Pinene from French oil of turpentine. They are, however, not chemically pure. If pinene nitrosochloride, easily obtained pure, be prepared from these modifications, and be then transposed with aniline, chemically pure inactive pinene will be obtained. Its properties will be similar to those above indicated.

Pinene contains one double linkage. It unites with 2Cl or 2Br, forming compounds,

which change on heating to p-cymene and halogen hydrides.

The dibromide crystallizes and melts at 170°. Zinc dust converts it into a terpene, melting at 65°, and isomeric with pinene and camphene; it apparently does not contain a double linkage (C. 1897, I, 1055). Pinene can be changed to camphene by means of concentrated sulphuric acid, or through its haloid acid addition products. It becomes dipentene when heated to 250-270°. Moist haloid acids convert pinene into dipentene dihydrohaloids (p. 311). Terpine hydrate is probably an intermediate product; it is formed when dilute nitric acid or sulphuric acid acts upon pinene.

d-Pinene Hydrochloride, Artificial Camphor, C₁₀H₁₇Cl, melting at 125° and boil-

d-Pinene Hydrochloride, Artificial Camphor, $C_{10}H_{17}Cl$, melting at 125° and boiling at 208°, is formed on conducting dry hydrochloric acid gas into well-cooled pinene. It is a white crystalline mass, with an odor like that of camphor. The hydrochloride from d-pinene is optically inactive, while the 1-pinene hydrochloride is lævo-rotatory [a]_D = -30°. Pinene Hydrobromide melts at 40° (A. 227, 282). Camphene results

from the splitting-off of hydrogen chloride or bromide.

Pinene Nitrosochloride, melting at 103°, is obtained by means of nitrosyl chloride, or amyl nitrite, glacial acetic acid, and hydrochloric acid. Hydrogen chloride in ether, when allowed to stand in contact with it, produces, just like limonene nitrosochloride (p. 311), hydrochlorcarvoxime (B. 29, 12). Pinene Nitrosobromide melts at 92°. The bases readily change the pinene nitrosobromides into inactive nitrolamines. Sodium and alcohol reduce pinene nitrosochloride to Nitrosopinene, C₁₀I₁₄: N. OH, melting at 132° (B. 28, 646), which yields pinylamine, C₁₀H₁₅. NH₂, by the action of zinc-dust and acetic acid.

The oxidation products of pinene have been studied quite thoroughly. Turpentine exposed to the air absorbs oxygen gradually, with the production of ozone. It resinifies at the same time with the formation of formic acid, acetic acid, and cymene in slight amount. See p. 325 for the production of pinol hydrate with the assistance of sunlight. Energetic oxidants, like nitric acid, produce terebic acid (p. 324), p-toluic acid, terephthalic acid, etc. Terpenylic acid is the chief product when the chromic acid mixture is the oxidant.

When pinene is carefully oxidized with potassium permanganate, pinene glycol is the immediate result, but the chief product resulting therefrom is Pinonic Acid, $C_{10}H_{16}O_3$, melting at 104° and boiling at 187° (15 mm.). It is a ketone-carboxylic acid. Other products are pinoyl formic acid, $C_{10}H_{16}O_4$, melting at 79°, a ketone-dicarboxylic acid, and nopic acid, $C_{10}H_{16}O_3$, melting at 127°, which sulphuric acid converts into dihydrocuminic acid (B. 29, 1923).

Pinonic acid is readily attacked. Bromine and alkali, or dilute nitric acid, oxidize it to the very stable pinic acid, $C_0H_{14}O_4$, melting at 102°. The latter acid, by means of the a-brom- and a-oxypinic acids, and oxidation of the last, give rise to norpinic acid, $C_{18}H_{12}O_4$, melting at 174°. The last two very stable acids very probably contain a tetramethylene ring corresponding to the formulas:

$$\begin{array}{ccc} \text{COOH.CH} < & \text{CH}_{C} & \text{CH}_{3} \\ \text{Pinic Acid} & \text{CHCH}_{2} \text{CO}_{2} \text{H} & \text{COOH.CH} < & \text{CII}_{3} \\ \text{Norpinic Acid.} & \text{Norpinic Acid.} \end{array}$$

Baeyer, therefore, concurring with Wagner, assumes that in pinonic acid and pinene there is present a four-membered ring—a so-called picean ring (B. 29, 2776):

$$CH_3$$
. CH
 CH_4
 CH_5
 CH_5
 CH_5
 CH_6
 CH_7
 CH_7
 CH_8
 C

The breaking-down of pinonic acid and pinoyl formic acid has also been attained in two other ways:

(1) Chromic acid changes pinonic acid to ketoisocamphoric acid, $C_{10}II_{17}O_5$, which is produced by the oxidation of campholenic acid (p. 328). Keto-isocamphoric acid can be broken down into isocamphoronic acid, $C_2II_{15}O_6$, and further into dimethyltricarballylic acid, COOH. C(CH₂)₂CH(COOH)CH₂COOH. The constitution of the latter has been proved by the decomposition of the corresponding oxy-acid into dimethyl succinic acid and oxalic acid when it is fused with caustic potash (compare oxycamphoronic acid, p. 333). The constitutional formulas of ketoisocamphoric acid, isocamphoronic

acid, and, therefore, that of pinonic acid, are at present subjects of controversy (see B. 29.

2779, 3027).

(2) When pinonic acid is heated with acids there occurs an intermediate hydrolytic decomposition, followed by a rearrangement into Homoterpenylic Methyl Ketone,

[Methoethylheptanonolide], (CH₁)2 C. CH. CH₂. COO CH₂. CH₃. CO. CH₃, a substance which we have already learned was a decomposition product of terpinol (p. 316). Pinoylformic acid is

similarly rearranged to Homoterpenoylformic Acid, (CH₂), C.CH. CH₂. COO CH..CH..CO.COOH. These rearrangement products upon further oxidation yield (B. 29, 2775):

Terebic Acid, C₁H₁₀O₄, melting at 175°, was first obtained by oxidizing turpentise oil with nitric acid; it is also produced in the oxidation of terpenylic acid with potssium permanganate (B. 29, 933). It behaves analogously to the paraconic acids. When heated it loses carbon dioxide and becomes proterbic acid, (CH₂), C: CHCH₂COOH, together with isocaprolactone and teraconic acid, (CH₂)₂C: C(COOII)CH₃. COOH, from which it can be re-formed by digestion with mineral acids. Baryta-water converts terebic acid into the crystallizing barium salt of diaterebic acid or oxyisopropyl-succinic acid. See p. 319 for the formation of terebic acid from caronic acid.

Terpenylic Acid, C₈H₁₃O₄, melts at 90° when anhydrous. It is obtained by oxidizing turpentine oil with a chromic acid mixture and homoterpenylic acid with nitric acid (B. 29, 2789). Upon distillation it yields Teracrylic Acid, (CH3), C: CH(CH3) CH, COOH. Terpenylic acid, by reduction, becomes β-isopropylglutaric acid (see

B. 29, 920, 2621). See p. 320 for aryterpenylic acid.

Homoterpenylic Acid, C₉H₁₄O₄, melting at 102°, results when homoterpenylformic acid is oxidized with nitric acid or with lead oxide (B. 29, 1916).

The oxidation of pinene to pinonic acid and the hydrolytic rearrangement of the latter to homoterpenylic methyl ketone is certainly to be regarded as the reverse of the processes which take place in the hydrolytic rearrangement of pinene into terpine hydrate, terpineol (p. 316), and the oxidizing decomposition of the latter into homoterpenylic methyl ketone (above).

Fenchene, $C_{10}II_{16}$, boiling at 158-160°, with sp. gr. 0.864, $n_D = 1.469$, is optically inactive, and is formed on digesting fenchyl alcohol with potassium sulphate, or fenchyl chloride with aniline (A. 284, 333). Fenchene can take up two bromine atoms. It is

only attacked by nitric acid when heat is applied.

Tetrahydrofenchene, C₁₀H₂₀, boiling at 160-165°, with sp. gr. 0.7945 (22°), n_D = 1.4370, is produced when fenchone and fenchyl alcohol are heated with hydriodic acid. Dihydrofencholene, C₉II₁₈—see fencholenic acid, p. 334.

2. Alcohols.—A. Monacid Alcohols: Borneo Camphor, Borneol, Camphol, C₁₀H₁₇OH, melting at 203° and boiling at 212°, occurs in three modifications in nature. d-Borneol is found in Dryobalanops camphora, a tree growing in Borneo and Sumatra, also in rosamary oil. 1-Borneol and inactive borneol are present in the so-called baldrianic camphor. Many wood-spines contain it in the form of a fatty acid ester, more especially the acetic ester.

Borneol is very similar to Japan camphor, but has an odor at the same time resembling that of pepper. It sublimes very readily. d- and l-Borneol are formed simultaneously from camphor by reduction with sodium and alcohol (A. 230, 225). Nitric acid oxidizes them to camphor. When borneol is heated with potassium bisulphate it breaks down into water and camphene (p. 321).

The methyl ether boils at 194° and the ethyl ether at 204° (B. 24, 3713). The acetyl ester melts at 29°. It consists of rhombic, hemihedral forms. It boils at 98° (10 mm.), $n_D = 1.46635$, $[a]_D = +38°$ 20′.

Bornyl Chloride melts at 148°. It results on treating borneol with PCl₅. Cam-

phene is formed when it splits off hydrochloric acid.

Isoborneol, C₁₀H₁₇OH, melting at 212°, is even more volatile than borneol. It is

produced when its acetate is saponified with alcoholic potash.

produced when its acetate is saponited with alcoholic potasn.

Its acetate, boiling at 107° (13 mm.), results upon digesting camphene and glacial acetic acid with concentrated sulphuric acid at 50-60° (D. R. P., 67255) (B. 27, R. 102).

Camphol Alcohol, C₁₀H₁₀OII, boiling at 203°, is produced when campholamine hydrochloride (p. 326) is acted upon with silver nitrite (B. 27, R. 126).

Camphel Alcohol, C₂H₁₁OII, melting at 25° and boiling at 179°, results from the interaction of camphelamine hydrochloride (p. 326) and silver nitrite. It is a tertiary alcohol. It readily decomposes into water and the hydrocarbon, C₂II₁₆ (B. 27, R. 126).

Fenchyl Alcohol, C₁₀H₁₇. Oll, melting at 45° and boiling at 201°, with sp. gr. 0.933, is produced in two modifications: by the reduction of d- and 1-fenchone (p. 333). has a penetrating and very disagreeable odor. d-Fenchyl alcohol, $[a]_D = + 10^{\circ} 36'$, is obtained from 1-fenchone, and 1-fenchyl alcohol, $[a]_D = -10^\circ$ 35', from d-fenchone (A. 284, 331). See also tetrahydrofenchol.

Fenchyl Chloride, C₁₀H₁₁Cl, boiling at 85° (14 mm.), is produced when phosphorus pentachloride acts upon fenchyl alcohol. See fenchene.

Isofencholen Alcohol, $C_{10}H_{17}OH$, boiling at 218°, with sp. gr. 0.927 (20°), $n_D =$ 1.476, is produced when alcohol and sodium act upon fencholen amide (p. 333) (A. 284, 337). It is readily attacked by potassium permanganate. When heated with dilute sulphuric acid it changes to Fenchenol, C₁₀H₁₈O, boiling at 183°, with sp. gr. 0.925 (20°), n_D = 1.46108. This compound, with the exception of the boiling point, can not be distinguished from cineol.

B. Polyacid Alcohols: Camphene Glycol, C₁₀H₁₆(OH)₂, melting at 192° and obtained from camphene by action of KMnO₄ (B. 23, 2311), is converted by IICl into an oxide isomeric with camphor (probably camphenilan aldehyde, p. 322).

Pinene Glycol, C₁₀H₁₆(OH)₂, boiling at 145-147° (14 mm.), and obtained from pinene with KMnO, by the addition of hydroxyl groups to the unsaturated union, is con-

verted by hydrochloric acid into pinol (B. 27, 2270).

Pinol Hydrate, Sobrevol, $C_{10}H_{16}(OH)_2$, is known in three modifications. d-Pinol Hydrate, melting at 150°, $[a]_D = +150^\circ$, and l-Pinol Hydrate, melting at 150°, $[a]_D = -150^\circ$, are produced when dextro- and lævo- turpentine oil are oxidized in the air on exposure to sunlight. [d+1]-Pinol hydrate results on treating pinol with hydrobromic acid and alkali, as well as upon mixing equimolecular quantities of d- and 1-pinol hydrates. Pinol hydrate is an unsaturated compound. Bromine converts it into a dibromide, melting at 131°. Potassium permanganate changes it to a tetra-acid

alcohol, Sobreritrite, $C_{10}H_{16}(OH)_4$, melting at 156° (B. 29, 1195, R. 587).

Pinol, [d+1]-Sobrerone, $C_{10}H_{16}(O,b)$ biling at 183°, with sp. gr. 0.953 (20°), $n_D = 1.46949$, is optically inactive. It is formed when the three pinol hydrates are treated with dilute sulphuric acid, and from the dibromide of terpineol (p. 316) by the splitting-off of 2HBr. It is as indifferent as cineol (p. 315) toward hydroxylamine, phenylhydrazine, and acid chlorides. This, as well as its formation from terpineol dibromide, is

represented in the following formula:

$$CH_3 \cdot CBr \xrightarrow{CHBr \cdot CH_2} CH \cdot C(OH)(CH_3)_2 \longrightarrow CH_3C \xrightarrow{CH \cdot CH_2} CH \cdot C(CH_3)_3$$

$$CH_3 \cdot CBr \xrightarrow{CH_3 - CH_3} CH \cdot C(OH)(CH_3)_2 \longrightarrow CH_3C \xrightarrow{CH \cdot CH_2} CH \cdot C(CH_3)_3$$

$$CH_3 \cdot CBr \xrightarrow{CH_3 - CH_3} CH \cdot C(OH)(CH_3)_2 \longrightarrow CH_3C \xrightarrow{CH_3 - CH_3} CH \cdot C(CH_3)_3$$

$$CH_3 \cdot CBr \xrightarrow{CH_3 - CH_3} CH \cdot C(OH)(CH_3)_2 \longrightarrow CH_3C \xrightarrow{CH_3 - CH_3} CH \cdot C(CH_3)_3$$

Pinol hydrate is a hydrate corresponding to this oxide, an oxyterpineol, which re-

Pinol nytrate is a hydrate corresponding to this oxide, an oxyterpineol, which is sults from pinene by the rupture of the picean ring (p. 323).

Pinol Dibromide, C₁₀l₁₆Br₂O, melting at 94° and boiling at 143° (11 mm.), is coverted by sodium or alcoholic potash into pinol. Formic acid reduces it to cymene (A. 268, 225). Pinol nitrosochloride, C₁₀H₁₆O. NOCl, melting at 103°, forms nitrolamines with bases. Pinol Glycol, C₁₆H₁₆O(OH)₂, melting at 125°, is obtained from pinol dibromide with silver oxide or lead hydroxide, or from its disactate, melting at 97° (a. 268, 202). (A. 268, 223). An apparently isomeric glycol is produced in the exidation of pinel with KMnO₄ (B. 28, 2710).

Camphor Pinacone, C, H₂₄O₂, melting at 1760, is formed, along with borneol, in the

reduction of camphor (B. 27, 2348; see also B. 29, R. 675).

3. Amines have been obtained by the reduction of nitrosopinenes, oximes, and

nitriles, as well as ketones with ammonium formate.

Bornylamine, C₁₀H₁₇. NH₂, melts at 159° and boils at 199°. The formyl compound is produced when camphor is heated with ammonium formate, and the base itself by the reduction of camphor and piperidine. Formyl- and Acetyl-bornylamine melt at 61° and 141°. When heated to 200-210° with acetic anhydride they break down, with the production of camphene (A. 269, 347). Camphylamine, C_bH₁₅. CH₁. NI₁, boiling at 194-196°, is produced when the nitrile of campholenic acid is reduced. The benzoyl compound melts at 77° (B. 20, 485; 21, 1128).

Campholamine, C₁₀H₁₉. NH₂, and Camphelamine, C₈H₁₇NH₂,—see campholic

acid (p. 328).

Fenchylamine and fencholenamine sustain the same relation to each other that we

observed in bornylamine and camphylamine.

Fenchylamine, C₁₀II₁₇NII₂, boiling at 195°, with sp. gr. 0.9095 (22°), is known in three modifications, produced from the corresponding fenchones on heating them with ammonium carbonate, or by reducing the fenchone oximes. d.Fenchylamine, [a] ... — 24.89°, is obtained from d-fenchone. The optical rotatory power of a series of derivatives has been studied:

Formyl-, Acetyl-, Propionyl-, Butyryl Fenchylamines, $[a]_D = 36.56^\circ$,

— 46.62°, — 53.16°, 53.11° (A. 276, 317).

Fencholenamine, C₂II₁₅. CH₂. NH₂, boiling at 110-115° (21-24 mm.), results from the reduction of the nitrile of fencholenic acid (A. 263, 138).

Pinylamine, C₁₀H₁₅. NH₂, boiling at 207° (760 mm.), 98° (20 mm.), with 0.943, is produced in the reduction of nitrosopinene (p. 323) (A. 268, 197). Nitrous acid con-

verts pinylamine into isocarveol (p. 317), a secondary alcohol.

Amidoterebenthene, $C_{10}II_{15}$. NH₂, boiling at 197-200° (760 mm.), is formed in the reduction of the decomposable nitroterebenthene, the product obtained when nitrous acid acts upon oil of turpentine. Its hydrochloride, $[a]_D = -48.5^\circ$, is lævo-rotatory, it being immaterial whether we proceed from the dextro- or lævo-rotatory turpentine oil (B. 22, R. 108; 24, R. 204).

4. Ketones. - Various transformation products of the ketones, C₁₀H₁₆O, camphor and fenchone, have been treated in the preceding These ketones are similar in their chemical behavior, but are apparently different in constitution. By reduction they yield horneol and fenchyl alcohol, from which they are conversely again obtained by oxidation.

Phosphoric anhydride dehydrates them, and thus camphor yields pcymene; and fenchone, m-cymene:

$$\begin{array}{ccc} \text{Borneol} & \stackrel{2H}{\longleftarrow} & \text{Camphor} & \stackrel{-H_2O}{\longrightarrow} & \text{p-Cymene} \\ \text{Fenchyl Alcohol} & \stackrel{-H_2O}{\longleftarrow} & \text{m-Cymene.} \end{array}$$

Camphor is known in two optically active and one optically inactive modification, while fenchone is known in two optically active forms.

d-Camphor, Common Camphor, Japan Camphor, $C_{10}H_{16}O$, melting at 175° and boiling at 204°, with $[a]_D = +$ 44.22° in alcohol (A. 250, 352), is found in the camphor tree (Laurus camphora). It is obtained by distillation with steam and sublimation. It is prepared artificially by oxidizing borneol with nitric acid and camphene with chromic acid. It is a colorless, transparent mass, crystallizes from alcohol, and sublimes in shining prisms of sp. gr. 0.985. It is very volatile, and is applied therapeutically. Its alcoholic solution is dextro-rotatory. Camphor yields pure cymene (p. 56) if distilled with P_2O_5 , and on boiling with iodine forms carvacrol, $C_{10}H_{14}O$ (p. 145). When boiled with nitric acid it yields different acids, chiefly camphoric and camphoronic acids. Upon reduction it passes into borneol (p. 324).

1-Camphor, Matricaria Camphor, is contained in the oil of *Matricaria Parthenium*. It resembles d-camphor even to the rotatory power $[a]_D = -44.22^\circ$. It yields l-camphoric acid upon oxidation.

(d + 1)-Camphor, melting at 178.6°, is produced on mixing d- and 1-camphors, and by the oxidation of i-borneol and i-camphene with chromic acid (B. 12, 1756).

Constitution of Camphor.—The camphor formula (1) proposed by Kekulé (1873) satisfactorily accounted for the change of camphor into p-cymene and carvacrol. However, the ready anhydride formation of camphoric acid, which had led to a seven-membered ring, could not be brought by it into accord with the known experiences relating to the anhydride formation of aliphatic dicarboxylic acids. The lack of additive power also remained unexplained. The formulas of Kanonnikoff and Bredt explained these relations far better. In them the p-carbon atoms of the hexagon of camphor were brought in direct union. The anhydride formation of camphoric acid, thus made parallel with ethylene succinic acid, could be understood on the basis of this formula. Baeyer (1893) showed that as camphoric anhydride melted higher than its hydrate, it probably contained an n-glutaric acid anhydride ring (A. 276, 265).

Camphoric acid is not the only oxidation product of camphor, for when it is further oxidized camphanic acid and camphoronic acid are produced. In the latter acid J. Bredt recognized a, \(\beta\)-trimethyltricarballylic acid, inasmuch as it decomposed, upon the application of heat, into trimethyl succinic anhydride, isobutyric acid, carbonic acid, water and carbon; whereas when camphoronic acid, the lactone of oxycamphoronic acid, obtained from it, is fused with caustic potash, trimethyl succinic acid and oxalic acid are produced very readily. Bredt concludes from this deportment that the carbon grouping of camphoronic acid, as well as that of trimethyl succinic acid, must be present in camphanic acid, camphoric acid, and camphor. The formula of Bredt (1893) may be imagined (B. 26, 3047) to have been evolved from that of Kekulé by rotating the isopropyl group about 180°, until it lies within the hexagon, and then its middle carbon atom is allowed to unite the two p-carbon atoms of the hexagon by the migration of an H atom and the dissolution of the double union:

The position of the CO-group is proved by the conversion of camphor into carvacrol (above).

The oxidation of camphor (1) to camphoric acid (2), camphanic acid (3), and campho-

ronic acid (4), as well as the decomposition of the latter into trimethyl succinic acid (5), also found among the oxidation products of camphor (B. 26, 2337), is represented in the following diagram:

The partial synthesis of camphor by the distillation of calcium homocamphorate harmonizes with this conception of the constitution of camphor (Ch. Z., 1895, 19, 1755).

New formulas for borneol, camphene, and many other derivatives closely related to

camphor, can be deduced from the camphor formula.

Transposition Products of Camphor.—Chlorine and bromine convert camphor into mono- and disubstitution products. a- and β_i d-Chlor-camphor melt at 92° and 100°. a and β-Dichlor-camphor melt at 93° and 77°, while a and β-Brom-camphor melt at 70° and 61°. Consult C., 1897, I, 601, for the action of sodium upon brom-campbor: Dicamphor, $(C_{10}H_{15}O)_2$, etc.

PCl₅ converts camphor into Camphor-dichloride (A. 19, 259), melting at 155°.

Two Chlornitrocamphors (a and β) are produced when chlorcamphor is digested with nitric acid; the copper and zinc couple reduces them to a- and β -nitrocamphor (B. 22, R. 266; 23, R. 115; 29, R. 270).

See B. 28, R. 643; 29, R. 512, for the camphor-sulphonic acids and their transforms-

Camphoroxime, C₁₀II₁₆: NOH, melts at 118° and boils at 249° (A. 259, 331). Its odor resembles that of camphor. See B. 29, R. 1107, for its preparation. Bornylamine is formed in its reduction (p. 326). Camphorsemicarbasone, C10H16: N. NH. CO. NHp melts at 237° (B. 28, 2191).

Camphorimine, C₁₀II₁₆: NII,—see B. 29, 2807; C., 1897, I, 814.
Campholic Acid, C₁₀II₁₇. CO₂II, melting at 95°, is formed when camphor is heated with sodium in xylene (B. 28, R. 376), or from sodium-camphor at 288°. Boiling nitric acid oxidizes it to camphoric and camphoronic acids (B. 27, R. 752). The amide melts at 79°. The nitrile melts at 72° and boils at 218°. It yields campholamine, C₁₀H₁₉NH₂, melting at 210°, upon reduction. Bromine and caustic alkali change the amide to Camphelylisocyanate, boiling at 201°, from which Camphelamine, C₂N₁₁NH₂, melting at 43° and boiling at 175° , is obtained (B. 26, R. 21; 27, R. 126). Isocampholic Acid, B. 29, R. 356. The camphor-ring in camphoroxime can be very easily ruptured by mineral acids, the products being a and β -campholene nitrile, isoaminocamphor, and dihydrocampholene lactone.

СН, - $| > C(CH_1)_2 |$, boils at 256°. Its sp. gr. $CH = C - CH_3 | COOH$ a-Campholenic Acid,

equals 0.992 (19°). It is optically active, n_D = 1.47125. The nitrile, b. p. 226°, of this acid is produced with water exit when dilute sulphuric acid acts upon camphoroxime. The reduction of the nitrile produces a Camphylamine, C₁₀H₁₇NH₂, boiling at 195°. Alcoholic potash saponifies it to a campholamide, melting at 130°, and finally to the acid. The latter is oxidized by potassium permanganate to:

a Dioxyhydrocampholenic Acid, C₂H₁₅(OH)₂CO₂H, melting at 144°, and a ketonic acid, l-Pinonic Acid, which affords decomposition products similar to those of the like-named oxidation product of pinene (p. 324). Chromic acid oxidizes a-campholen- or dihydrodioxycampholenic acid to Isoketocamphoric Acid, $C_{10}H_{10}O_5 = CH_3$. CO. $C(CH_3)_0CH(CH_4COOH)_2$ (?), and eventually to Isocamphoronic Acid, $CO_3HC_4CH(CH_4COOH)_3$ (?), m. p. 167°. Concentrated suphuric acid, when warmed with the latter that acts for CO and temporalis acid results (R. 90, 2006).

with the latter body, sets free CO₂, and terpenylic acid results (B. 29, 3006).

β-Campholenic Acid, melting at 52° and boiling at 245°, is optically inactive. Its mitrile, boiling at 220-230°, is produced in the action of stronger acids (concentrated HI) upon camphoroxime. It is reduced to β -camphylamine, melting at 197°, which may be saponified to an *amide*, melting at 86°. Potassium permanganate oxidizes β -campholenic acid to a dihydroxy-acid, melting at 146°, and with it an oily acid which readily changes to *isocamphorone*, C₂H₁O, boiling at 217°. Chromic acid oxidizes the β -acid to γ -acetylisocapronic acid, CH₂, CO. C(CH₂)₂CH₂CH₂COOH, melting at 48°. Further oxidation leads to a decomposition into a-dimethylglutaric acid and a-dimethylsuccinic acid. The same decomposition products are obtained from isocamphorone (B. 30, 242). The conversion of β -campholenic acid, when heated with bromine, into I, 3,4-xylyl-acetic acid (B. 29, R. 643) is peculiar.

CH₂—CH

Dihydrocampholene Lactone, CH₂—CH₃—CH₃, melting at 30° and CH₂—C(CH₃)—O—CO boiling at 256°, appears as the principal or the by-product in the decompositions of

camphoroxime by strong acids, and may be obtained by acids from the two campholenic acids, as well as from isoaminocamphor. Chromic acid oxidizes it to oxydihydrocam-

pholene lactone, melting at 144° (B. 30, 404).

Isoamino-camphor, C₁₀H₁₇ON, boiling at 254° (760 mm.), 152° (65 mm.), is formed along with the preceding bodies when stronger acids act upon camphoroxime, campholenamides, and nitriles. It apparently contains a primary amine group, and is very similar to the isomeric amido-camphor (p. 330). It changes quite readily to dihy-

drocampholenolactone. Compare B. 30, 324, for its constitution. $CH - CH(CH_3)$ $CH = C(CH_3)$ $CH = C(CH_3)$ $CH = C(CH_3)$ $CH = C(CH_3)$ $CH_3 - CH(CH_3)$ $CH_4 - CH(CH_3)$ $CH_3 - CH(CH_$

ing at 134°, is produced when a- or, better, β -campholenic acid has been heated. Carbon dioxide is eliminated. It is, further, formed when P₁O₅ acts upon the chloride of campholic acid. The dibromide melts at 97°. Campholene, heated with HI-acid to 280°, becomes hexahydropseudocumene, just as β campholenic acid changes to xylyl-acetic

acid (B. 30, 594), and camphoric acid to tetrahydroisoxylene (B. 26, 3053).

An apparently isomeric Campholene, C₀H₁₆ boiling at 137°, has been obtained together with carvacrol from chlor-camphor by the action of zinc chloride (B. 26, R.

Nitrous acid, or sodium bisulphite and boiling dilute sulphuric acid, act upon isonitrisocamphor, and the product is camphor-quinone, which is also formed in the oxidation of cam-

phocarboxylic acid (B. 27, 1447). Camphor-quinone, $C_8H_{14} \stackrel{CO}{<_{CO}}$, resembles quinone and the a-diketones. Its odor is peculiarly sweet. It volatilizes with aqueous vapor and sublimes at 60° in golden yellow needles that melt at 198° (A. 274, 71).

Zinc-dust and hydrochloric acid or aluminium amalgam reduce it to a-Oxycam-

phor, C₈H₁₄ CH OH , melting at 203-205°, which may be reoxidized to camphorquinone. The latter, under the influence of various reagents, changes to derivatives of camphoric acid (compare B. 30, 657, 659).

Isonitroso-camphor, C₈H₁₆CO is obtained by the action of amyl nitrite and

sodium ethylate upon camphor. The compound melts at 153°. Concentrated sulphuric acid converts it into the imide of camphoric acid (B. 26, 241), while acetyl chloride, PCl_a or soda and acetic anhydride change it to the mono-nitrile of camphoric acid (B. 29, R. 651). Zinc and dilute acids reduce it to amido-camphor (A. 274, 71).

Camphor-dioximes—a-dioxime, m. p. 181°; β-dioxime, m. p. 220°—result on treat-

ing isonitroso-camphor with hydroxylamine acetate. y-Diaxime, m. p. 131°, is made by treating isonitroso-camphor with free hydroxylamine (B. 26, 243). An isomeride of the camphor dioxime is-

Pernitroso-camphor, C₁₀H₁₆N₂O₂, melting at 43°, which results from the interaction of nitrous acid and camphoroxime, and changes, upon treatment with concentrated suphuric acid, to Isocamphor, C₁₀H₁₆O (B. 29, R. 1106).

Amido-camphor, C₈H₁₄CO , boiling at 244°, is produced when isonitroso-

camphor is reduced. It is a paraffin-like mass; it has a fishy odor. Its hydrochloride, melting at 224°, acts similarly to, although not so powerfully as, curare. Its acetyl derivative melts at 108° (A. 274, 91).

Azocamphor, Monoketazocamphor-quinone, C₈H₁₄ C N, melts at 74°.

yellow-colored crystals. It is produced when nitrous acid acts upon the hydrochloride of amido-camphor (B. 26, 1718). Potassium sulphite changes it to a hydrazine-sulphonate, which concentrated hydrochloric acid decomposes into hydrazine and camphorquinone (B. 29, R. 1115).

CH₃—C

CH

azocamphenone, when azocamphor is heated. It has an odor like that of camphor. Its oxime melts at 132° (B. 27, R. 590). Consult B. 29, R. 1108, for the action of bromine and hydrogen bromide.

sodium or sodium ethylate and formic ester act upon camphor (A. 281, 306). Hydroxylamine changes oxymethylene camphor into the oxime of formylcamphor and cyancamphor.

Chlormethylene-camphor, C_8H_{14} $\stackrel{C}{\underset{CO}{\text{CO}}}$ = CHCl, boiling at 119° (16 mm.), is produced when PCl₃ acts upon oxymethylene-camphor.

Oxymethylene-camphor Anhydride, $[(C_8H_{14}CO) = CH]_9O$, melting at 188°, is

obtained from the sodium salt of oxymethylene-camphor and chlormethylene-camphor.

The methyl ether, (C₁₀H₁₄O) = CHOCH₃, melting at 40° and boiling at 262°, is obtained (1) from oxymethylene-camphor, sodium ethylate, and methyl iodide, (2) from chlormethylene-camphor and sodium methylate, and (3) from oxymethylene-camphor, methyl alcohol, and hydrochloric acid. The accetate, (C₁₀H₁₄O) = CH · O · CO · CH₃, melting at 63° and boiling at 290-293°, is obtained from oxymethylene-camphor and acetic anhydride.

Oxymethylene-camphor Cyanhydrin, C₈H_H CH . CH(OH)CN melting at 2°, is formed from oxymethylene

122°, is formed from oxymethylene-camphor, glacial acetic acid, and potassium cyanide. When boiled with acetic anhydride it yields-

Cyanmethylene-camphor, $C_8H_{14}\begin{pmatrix} C = CII.CN\\ CO \end{pmatrix}$, melting at 46° and boiling at

280°. Hydrochloric acid converts it, when heated to 120° in glacial acetic acid solution, into Camphor-methylene Carboxylic Acid, $C_8H_{14} \subset C = CH \cdot CO_2H$, melting at 101°.

d-Camphor-carboxylic Acid, C_8H_{11} CH. CO_2H , melts, with carbon dioxide evo-

hation, at 128°. It is obtained from sodium camphor and carbonic acid (B. 24, 3382). Its esters yield sodium compounds, which, heated with alkylogens, produce alkyl-camphocerboxylic esters, whose acids, when heated, evolve carbon dioxide and break down into alkyl-camphor.

d-Cyan-camphor, C₈H₁₄CO, melting at 127°, is produced when cyanogen

is conducted into sodium camphor, and by digesting a solution of sodium oxymethylenecamphor with hydroxylamine hydrochloride (A. 281, 349). Alkalies and alkylogens convert it into alkyl-cyan-camphor.

Camphoric Acid.—There are four optically active and two inactive

camphoric acids.

d-Camphoric Acid, ordinary camphoric acid (Constitution, p. 328), $C_{0}H_{14}(CO_{2}H)_{2}$, m. p. 187°, $[a]_{D}=+49.7^{\circ}$ in alcohol, is obtained by heating d-camphor or campholic acid with nitric acid (A. 163, 323), and because it can be made without great trouble, has been exhaustively When it is heated above the melting point, or when treated with acetyl chloride (A. 226, 1), it changes to its anhydride, melting at 221° and boiling at 270°. The acid is dextro-rotatory.

By fusion with caustic potash, camphoric acid changes to isopropyl succinic acid and 1-isocamphoric acid; by oxidation with nitric acid, camphoronic acid and dinitrocapronic acid, CH₃. C(NO₂)₂, are produced, while with chromic acid the products are camphoronic (CH₂),C.CO,H and trimethyl succinic acids. Water and bromine change it to camphanic acid (B. 28,

2151). Compare B. 30, 289, for the oxidation of camphoric acid with potassium permanganate. The distillation of calcium camphorate yields Camphorphorone, $CH_3-C=C(CH_3)_3$ CH₃—CH(CH₃)₂. CO, boiling at 195-200°. It is oxidized by potassium permanganate

to a-methylglutaric acid (B. 26, 3053). Tetrahydro- and hexahydroisoxylene are pro-

duced when camphoric acid is heated with hydriodic acid.

The d-camphoric acid forms two series of acid esters: the allo-esters, produced by the partial saponification of the neutral esters, and the ortho-esters, resulting from the partial esterification of the acids (B. 26, 289).

See B. 26, 600, R. 87, 614, 688, for the electrolysis of the ester acids.

The dichloride, C₈H₁₄<CCl₂>O, boils at 140° (15 mm.) (B. 23, R. 229).

The diamide, $C_8H_{14}C_2O_2(NH_2)$, melting at 197°, is converted by potassium hypobromite into $C_{10}H_{16}N_2O_2$, melting at 235°. This is probably the ureide of an oxyacid (B. 27, R. 894) corresponding to campholactone. Two isomeric Camphor-aminoacids, melting at 177° and 180°, have been obtained from the anhydride with ammonia, and from the imide with sodium hydroxide (B. 29, R. 96).

The imide, C₅H₁₄C₂O₂NH, melting at 248° and boiling at 300°, is also formed from isonitrosocamphor (B. 26, 58, 242; A. 257, 308).

The methyl imide, C₅H₁₄C_{CO}>NCH₃, melting at 40-42°, is obtained from silver camphoronimide and methyl iodide, as well as by heating methyl isoimide above its melting point (B. 29, R. 96).

Methyl Isoimide, C₈H₁₆<C N. CH₈, melting at 134°, results when camphormethyl-amino-acid is treated with acetyl chloride or PCl₂ (B. 26, R. 688).

Camphoryl Hydroxylamine, C₈H₁₄< $^{CO}_{CO}>N$. OH, melts at 225° (B. 27, R. 893).

Camphor-nitrilo-acid, cyanlauronic acid, C₈H₁₄(CN)COOH, melting at 152°, is formed when campbor-amino-acid is treated with acetyl chloride and subsequently with ammonia, or by the interaction of acetyl chloride and isonitrosocamphor (p. 329 and B. 29, R. 651, 779).

1-Camphoric Acid results from the oxidation of matricaria camphor. It resembles

the d-variety in every particular, even to the rotatory power.

[d + 1] Camphoric Acid, Paracamphoric Acid, melting at 204°, is formed upon mixing alcoholic solutions of equimolecular quantities of d- and l-camphoric acids (B.

23, R. 229).

d-Isocamphoric Acid, d-cistrans-camphoric acid, melting at 171°, with [s]₀ = +48°, may be prepared by heating l-camphoric acid with water, or, better, with a mixture of glacial acetic acid and hydrochloric acid. It does not form a real anhydride, hence can be easily separated by means of acetyl chloride from the 1-camphoric acid.

1-Isocamphoric Acid, $[a]_D = -48^\circ$, is obtained from both d-camphoric acid and

its chloride.

[d+1]-Isocamphoric Acid, melting at 191°, results from the union of d-and l-isocamphoric acids. When they are bested the corresponding camphoric anhydrides are produced (B. 27, 2001). Compare B. 29, 1700, for the crystal forms of the camptonic

Brom-camphoric Anhydride (Constitution; see camphanic acid), CaHilBrO, melb at 215°.

Camphanic Acid, (CH₂),C , melting at 201°, is obtained on boiling -c(ch,), co

brom-camphoric anhydride with water. Nitric acid oxidizes it to camphorosic acid. By distillation camphanic acid loses carbon dioxide, and becomes campholactone and lauronolic acid (A. 227, I). Compare B. 29, R. 772, 861, for additional brom- and oxycamphoric acids.

Lauronolic Acid, C₈II₁₃. CO₂H, is a colorless oil. It is formed when soda acts on brom-camphoric anhydride. Upon standing, or by boiling in hydrochloric acid solution,

it rearranges itself to Campholactone, $C_8H_{14} \stackrel{CO}{\bigcirc}{}^{1}$, melting at 50° (A. 227, 5).

Isolauronolic Acid, C₈H₁₃. CO₂H, melting at 134°, is obtained from sulphocamphylic acid heated to 200°, as well as by the action of Al₂Cl₂ upon camphoric anhydride

(C., 1897, 1, 763). Sulphocamphylic Acid, Sulphocamphoric Acid, C₂H₁₆SO₄ + 2H₂O, melting at 160-165°, is produced in the action of sulphuric acid upon camphoric acid. Upon heat-

ing it changes to isolauronolic acid, and upon oxidation with nitric acid yields sulphoisopropyl-succinic acid and dimethylmalonic acid (B. 26, 2044).

Campholide, $C_8H_{14} < \frac{CH_2}{CO} > O$, melting at 211°, is formed in the reduction of camphoric anhydride with alcohol and sodium amalgam, just as phthalide is obtained from phthalic anhydride (B. 29, R. 221, 288). The lactam, C₈H₁₄<CH₂>NH, melting st 229°, being analogous to the phthalimidines, may be designated campholimidine. It results upon heating the hydrochloride of the corresponding amido-acid, produced in the reduction of camphor-nitrilo-acid (B. 29, 98, 652).

196-200°, is produced in the oxidation of camphene with dilute nitric acid. It forms an anhydride acid when it is heated. This melts at 205°. It subsequently splits off CO; and passes into the anhydride of-

CH, — CH — COOH $C(CH_3)_2$, melting at 204°. -CH - COOHApocamphoric Acid, Camphopyro-acid, It behaves analogously to camphoric acid (B. 29, R. 175, 773; Ch. Zt., 1896, p. 840).

d-Homocamphoric Acid, Hydroxycamphocarboxylic Acid, C₈H₁₄CH₂.COOH, melting at 234°, is produced when cyan-camphor is boiled with aqueous caustic potash. Its mononitrile is formed on heating campholide (see this) with potassium cyanide (B. 29, R. 288). d-Camphor is obtained on heating calcium homocamphorate in a current of carbon dioxide.

d-Hydro-camphorylacetic Acid, $C_0H_{14} < \frac{CH_2 \cdot CH_2 \cdot CO_2H}{CO_2H}$, melting at 142°, is produced when hydrocamphorylmalonic acid is heated (A. 257, 303).

produced when hydrocamphorylmalonic acid is heated (A. 257, 303).

d-Hydrocamphorylmalonic Acid, C₈H₁₄<CH₂. CH(CO₂H)₂, melting at 178°, is obtained by the reduction of camphorylmalonic ester (A. 257, 301).

d-Camphorylmalonic Ester, C_8H_{14} $C = C (CO_2\dot{C}_2H_5)_3$, melting at 82° and boiling at 274° (40 mm.), results from the action of sodium malonic ester upon the chloride of camphoric acid.

Camphoronic Acid, a,β-Trimethyltricarballylic Acid, (CH₂), C — C(CH₂) — CH₂ is produced in the oxidation of camphoric acid, camphanic acid, and campholic acid with nitric acid.

It has been synthesized in the following manner: acetoacetic ester and a-bromiso-butyric ester are condensed by zinc to β -oxy-a, β -trimethylglutaric ester, COOR. CII₂-C(OH)(CH₃)C. (CH₃)₂COOR, which PCl₃ converts into the ester of the β -chlor-acid, and the latter is then changed by potassium cyanide to the ester of β -cyan-a, β -trimethylglutaric acid, the mononitrile of camphoronic acid, which is then saponified to camphoronic acid (C., 1897, I, 813).

The importance of camphoronic acid in the determination of the constitution of camphor has been explained (p. 328). Camphoronic acid melts at 135°, changing at the same time into camphoro-anhydridic acid, melting at 135° and boiling at 205° (12 mm.). The chloride of the latter acid is converted by bromine into two isomeric bromcamphoro-anhydridic acid chlorides; one of these, when boiled with water, forms the lactone of unstable oxycamphoronic acid, camphoranic acid, while the other, under similar treatment, yields a stable oxycamphoronic acid, melting at 248°. Camphoronic acid, upon distillation, breaks down into trimethyl succinic anhydride, iso utyric acid, CO₂, H₂O, and carbon.

Camphoranic Acid, C₉H₁₂O₄ + H₂O, melting at 209°, is a lactonic acid which resists decomposition by alkalies very strongly. When fused with caustic potash it is readily split into trimethyl succinic acid and oxalic acid (privately communicated by J. Bredt):

with sp. gr. $0.9465(19^{\circ})$, $n_D=1.46306$, is known in two isomeric modifications. It is the ketone of all known ketone derivatives of the terpenes which is most like camphor in its behavior.

d-Fenchone, $[a]_D = +71.70^\circ$, was discovered in 1890 by Wallach and Hartmann, while 1-Fenchone, $[a]_D = -66.94^\circ$, was found in 1892 by Wallach, together with pinene and thujone or tanacetone, in the oil of thuja. It is very stable toward concentrated nitric acid. Potassium permanganate oxidizes it to dimethylmalonic acid. acetic

acid, and oxalic acid. When reduced it passes into d- and 1-fenchyl alcohol (p. 325) and tetrahydrofenchene (p. 324). With conditions analogous to those under which camphor yields p-cymene, fenchene will yield m-cymene—e. g., upon heating with P.O. Fenchone does not form an oxymethylene derivative.

Fenchonoxime, $C_{10}H_{16}$: NOH, melts at 161° and boils at 240°; $[a]_D = +65.94°$

(see B. 29, 2818).

Fencholenic Acid, C_0H_{15} . CO_2H , boiling at 260°, with sp. gr. 1.0045, $n_D=1.4766$, is obtained from its amide (a isofenchonoxime) and its nitrile (fenchonoxime anhydride) by saponitication with alcoholic potash. Hydriodic acid reduces it to dihydrofencholene, C₂H_{1s}, boiling at 140°, with sp. gr. 0.79 (20°), n_D = 1.43146. The amide (a-isofenchonexime), melting at 113°, results when the nitrile is acted upon with alcoholic potash. The nitrile (fenchonoxime anhydride), boiling at 217°, with sp. gr. 0.898 (20°), no 1.46108, $[a]_{D} = +43.31^{\circ}$, is produced on gently heating fenchonoxime with dilute sulphuric acid.

β-Isofenchonoxime, C₁₀H₁₇NO, melting at 137°, is formed when a-isofenchonoxime is boiled with dilute sulphuric acid. It is a monobasic body, probably a lactam (B. 28,

R. 456).

RESINS.

The resins are closely related to the terpenes, and occur with them in plants, and are also produced by their oxidation in the air. Their natural, thick solutions in the essential oils and turpentines are called balsams; whereas the true gum resins are amorphous, mostly vitreous bodies. Their solutions in alcohol, ether, or turpentine oils constitute the commercial varnishes.

Most natural resins appear to consist of a mixture of different, peculiar acids, the resin acids. The alkalies dissolve them, forming resin soaps, from which acids again precipitate the resin acids. By their fusion with alkalies we obtain different benzene derivatives (resorcinol, phloroglucin, protocatechnic acid); and when they are distilled with zinc-dust they yield benzenes, naphthalenes, etc.

Colophony is found in turpentine (p. 322) and, in the distillation of the latter, remains as a fused mass. It consists principally of Abietic Acid, C19H28O2 (Sylvic acid). which can be extracted by hot alcohol, crystallizes in leaslets, and melts at 139° (147°). When oxidized it yields trimellitic, isophthalic, and terebic acids.

Gallipot Resin, from Pinus maritima, contains pimaric acid, C₂₀II₂₀O₂, which is very similar to sylvic acid and passes into the latter when distilled in vacuo. It melts at 210°. The latest investigations show that pimaric acid consists of three isomerides

(B. 19, 2167).

Gum lac, obtained from East India fig trees, constitutes what is known as shellac when fused. This is employed in the preparation of sealing-wax and varnishes.

Amber is a fossil resin, found in peat-bogs. It consists of succinic acid, two resin acids, and a volatile oil. After fusion it dissolves easily in alcohol and turpentine oil, and serves for the preparation of varnishes.

To the gum resins, occurring mixed with vegetable gums, and gum in the juice of

plants, belong gamboge, euphorbium, asafœtida, caoutchouc, and gutta percha.

Caoutchouc, because of its wide applicability, is especially important. It has been obtained from tropical Euphorbiacere, Apocinacere, etc. In Brazil it is made from Siphonia elastica, in India from Ficus elastica, as well as other varieties of Ficus. Purified caoutchouc has the formula (C₀II_n) x. When distilled it yields isoprene, C₀II_s (see this), which polymerizes spontaneously to caoutchouc and also to dipentene. Caoutchouc takes up sulphur when it is thoroughly kneaded with it, or when it is treated with a mixture of S₂Cl₂ and CS₂ (B. 27, R. 204, 521, 601, 609, 701, 816; 29, R. 136).

The product is a vulcanized caoutchouc, which continues elastic within a considerable

range of temperature.

AROMATIC HYDROCARBONS CONTAINING SEVERAL NUCLEI.

A. PHENYLBENZENES AND POLYPHENYL-FATTY HYDROCAR-BONS.

Just as alkyl groups are joined to one another, or as they are introduced into benzene and its homologues, so the benzene hydrogen atoms can be replaced by phenyl-, tolyl-, benzyl-, and other hydrocarbon residues. The products are: (1) The phenylbenzenes, in which the benzene nuclei are in immediate union:

$$\begin{array}{cccc} C_6H_5 & C_6H_6 & C_8H_5 & C_6H_4 & CH_3 & C_6H_4/(C_6H_5)_3 & C_8H_3(C_6H_6)_8 \\ \text{Diphenyl} & \text{Phenyl Tolyl} & \text{Diphenyl Benzenes} & \text{Triphenyl Benzenes}. \end{array}$$

(2) The polyphenyl paraffins, olefines, and acetylenes, in which the benzene residues are held together by fatty hydrocarbons:

In addition to these groups we have: B. The aromatic hydrocarbons with condensed nuclei.

I. PHENYLBENZENE GROUP.

I A. Diphenyl Group.—The first or parent hydrocarbon of this

group is diphenyl or phenylbenzene.

Diphenyl, Phenylbenzene, Biphenyl, C₆H₅. C₆H₅, melting at 71° and boiling at 254°, is present in slight amount in coal tar. It is formed (1) upon conducting benzene vapors through tubes heated to redness (Berthelot, Z. f. Ch., 1866, 707; B. 9, 547; A. 230, 5); (2) in the action of sodium upon the solution of brombenzene in ether or benzene—higher, condensed hydrocarbons being produced at the same time (Fittig, A. 121, 363; B. 29, 115); (3) from diazobenzene chloride (a) by action of benzene and aluminium chloride, (b) with stannous chloride, (c) when alcohol and Cu-powder act upon diazobenzene sulphate, (d) from the latter salt and warm benzene (B. 23, 1226; 26, 1997).

If dissolved in glacial acetic acid and oxidized with chromic anhydride it yields benzoic acid. Metallic sodium reduces diphenyl, dissolved in amyl alcohol, to tetra hydrodiphenyl, C₁₂H₁₄, boiling at 245°. The latter readily forms a dibromide which alcoholic potash converts into dihydro-diphenyl, C₁₂H₁₂, boiling at 248° (B. 21, 846). A dihydrodiphenyl of melting point 66° has been obtained from phenyldihydroresorcinol (p. 297) by converting this diketone into the corresponding dihydric alcohol, and removing two molecules of water from the latter by means of phosphorus pentoxide (A. 289, 168). Fluorene (B. 19, R. 672) is formed when methylene chloride and aluminium chloride act upon diphenyl.

Alkylic Diphenyls have been obtained: (1) by the action of nitrous acid upon the alcoholic solution of their amido-compounds (B. 17, 468; 21, 1096; (2) from the action of sodium upon the brominated alkylbenzenes (B. 4, 396); (3) from diphenyl, chlor-alkyl,

or ethylene and aluminium chloride (B. 20, R. 218); (4) from aromatic diazochlo containing one nucleus (see p. 106). The position of the alkyl-groups is determine oxidation, if it has not been made evident by the components.

```
. . . . boils at 272-277°.
 m-Phenyltolyl, m-Methyl Diphenyl, . .
 p-Phenyltolyl (B. 26, 1996) (m. p. +3°), . . .
                                             " 263-267°.
                                                283°.
 m-Ethyl Diphenyl,
                                                286°.
                                             "
                                                286°.
o,m-Ditolyl, . . . .
 p. Ditolyl (B. 29, 114), m. p. 121°, is volatile without decomposition.
```

Diphenyl Substitution Products.—Each monosubstitution product of diphenyl exist theoretically in three isomeric forms. Chlorine, bromine, the NO₂ group, an sulpho-group prefer the p-position with reference to the point of union of the benzene residues. o- and o,p-Derivatives are formed together with the p- and r rivatives. The p_2 -derivatives, having two different substituents,—z. g., p-brom-p-diphenyl,—yield both p-brom- and p-nitrobenzoic acids when they are oxidized benzidine). The amidodiphenylenes, particularly benzidine, or p_2 -diamidodiphenyl the diphenyl sulphonic acids, afford, as in the case of the corresponding benzene de tives, numerous derivatives of diphenyl.

It is interesting to note that og disubstitution products are known in which a biv atom, O and S, or a bivalent group, NH, (CH2, CO), replaces two hydrogen atou the ortho-position with reference to the point of union of the two benzene nuclei.

The principal representatives of such diphenylene compounds are:

$$\begin{array}{c|cccc} C_6 II_4 & C_6 II_4$$

The first three will be treated in connection with the heterocyclic derivatives furfurane, thiophene, and pyrrol, from which they can also be derived. They are for by pyro-reactions from phenyl ether, phenyl sulphide, and diphenylamine.

Halogen Diphenyls.—o- and p-Chlordiphenyl melt at 34° and boil at 267°, an

75° and at 282°. o and p-Bromdiphenyls, liquid, boil at 297° and melts at 89°, boils at 310°. p₂. Dichlor-, p₃. Dibrom-, and p₄. Di-ioddiphenyls melt at 148° boil at 315°, at 164° and 357°, and melt at 202° (A. 207, 333).

Perchlordiphenyl, C₁₂Cl₁₀, does not melt at 270°. It is often produced in exh ive chlorinations (B. 16, 2881).

Nitro-diphenyls. - The nitration of diphenyl gives rise to o- and p-nitro-, as well . p₃· and o,p-dinitrodiphenyls. o₃· and m₂· Dinitro-diphenyls are obtained from benzi (B. 20, 1028). o- and p-Nitro-diphenyls melt at 37° and boil at 320°; at 113°

 o_2 , m_2 , p_3 , and o,p Dinitro-diphenyls melt at 124°, 197°, 233°, and 93°. p_2 o,p-Dinitro-diphenyl have also been obtained from sodium isodiazonitrobenzene and n benzene (B. 29, 165). p Brom-p-nitro-diphenyl melts at 173° (A. 174, 218).

Amido-diphenyls and Amido-ditolyls can be prepared by reduction of the corresponding nitro-compounds. The formation p₂-diamido-diphenyl by the rearrangement of its isomeride hydrazob zene (p. 117) is of great technical importance, because p₂-diami diphenyl or benzidine is a starting-out substance for the preparation substantive cotton dyes—dyes which unite directly with the cotton fi without the aid of mordants.

o-Amido-diphenyl, melting at 45°, is also obtained from o-phenylbenzamide means of bromine and caustic soda (A. 279, 266; B. 25, 1974). When condu over heated lime it forms carbazole. p-Amido-diphenyl, Xenylamine, melts at

and boils at 322° (A. 260, 233). p₂-Nitroamido-diphenyl, from p₂-dinitro-diphenyl, melts at 198°.

o₂-Diamido-diphenyl, melting at 81°, and m₂-Diamido-diphenyl have been obtained by reducing o₂- and m₂-dimitro-diphenyl. When o₂-diamido-diphenyl is heated with concentrated sulphuric acid it yields carbazole. Its tetrazochloride is changed by potassium sulphydrate to carbazole, and when its aqueous solution is heated diphenylene oxide is produced (B. 26, 1703). The reduction of the tetrazo-compound of o₂-dimitro-diphenylene oxide.

amido-diphenyl gives rise to Diphenylene o₂-dihydrazine, [6¹¹4[2]NHNH₂, melting at C₆H₄[2']NHNH₂.

110° (B. 29, 2270). When heated with hydrochloric acid at 150° it breaks down easily into ammonium chloride and an o₂-asodiphenylene, so called phenazone,

 $C_6H_4/N = N_{C_6H_4}$, which can also be directly obtained by the reduction of ogdinitro-diphenyl with sodium amalgam and methyl alcohol.

Phenazone will be treated at the conclusion of the ortho-diazines under the heterocyclic compounds.

Benzidine, p₁-Diamido-diphenyl, melting at 122° (Zinin, 1845), is obtained by the reduction of p₂-dinitro-diphenyl and p₃-nitroamido-diphenyl. It is technically prepared by the reduction of azobenzene in acid solution; the hydrazobenzene, formed at first, rearranges itself to benzidine and diphenyl, or 0,p-diamido-diphenyl. This is a remarkable reaction, to which attention has already been called in connection with hydrazobenzene (p. 117) (A. 207, 330).

The great insolubility of the sulphate in water affords a means of separating benzidine from diphenyline. When treated with concentrated sulphuric acid and nitric acid, one or two NO_2 -groups enter in the m-position with reference to the amido-groups of benzidine. The products are o-nitro-p₂-diamido-diphenyl and o₂-dinitro-p₃-diamido-diphenyl (B. 23, 794). m₂-Dinitro-p₂-diacetamido-diphenyl results on nitrating diacetbenzidine. The two nitro-compounds by removal of the amido-groups yield o₂- and m₃-dinitro-diphenyls (see these).

Constitution.—The p-position of the two amido-groups of benzidine (1) is evident from the oxidation of p₃-bromnitro-diphenyl to p-brom- and p-nitrobenzoic acids (5, 6), because benzidine (1) is formed from p₃-dinitro-diphenyl (2), which may be rearranged to p₃-amidonitro-diphenyl (3), and p₃-bromnitro-diphenyl (4) (Gustav Schultz, A. 174, 227):

$$\begin{array}{c} C_{6}H_{4}\overset{(1)}{[4]}NH_{2} & \xrightarrow{C_{6}H_{4}\overset{(2)}{[4]}NO_{2}} \xrightarrow{C_{6}H_{4}\overset{(3)}{[4]}NO_{2}} \xrightarrow{C_{6}H_{4}\overset{(4)}{[4]}NH_{2}} \xrightarrow{C_{6}H_{4}\overset{(4)}{[4]}NH_{2}} \xrightarrow{C_{0}H} \\ C_{6}H_{4}\overset{(4)}{[4]}NH_{2} & \xrightarrow{C_{6}H_{4}\overset{(4)}{[4]}NH_{2}} \xrightarrow{C_{0}H} \xrightarrow{C_{0}H} \\ C_{6}H_{4}\overset{(4)}{[4]}Br & \xrightarrow{C_{0}H} \end{array}$$

The constitution of benzidine forms the basis for *one* of the proofs of the constitution of diphenic acid (p. 340); also for that of phenanthrene isomeric with anthracene.

Benzidine Disulphate consists of small scales with a silvery luster; preparation, B. 26, R. 321. Concentrated sulphuric acid converts it into benzidine sulphone (B. 22, 2467).

Diacetbenzidine melts at 317°. Thionylbenzidine, (C₆H₄. NSO)₂ (B. 24, 753). Di-(o-nitrobenzyl)-benzidine melts at 227° with decomposition (B. 29, 1450).

o-Nitro-p₃-diamido-diphenyl, m-Nitrobenzidine, melts at 143° (B. 23, 796)—see

0₂-Dinitro-p₃-diamido-diphenyl, m-Dinitrobenzidine, melts at 214° (B. 23, 795). 3₃-Dinitro-4₃-diacetdiamido-diphenyl melts above 300° and is converted by caustic potash into 3₂-dinitro-4₃-diamido-diphenyl, o-dinitrobenzidine, melting at 220° (B. 5, 237; 20, 1024). 5₃-Dinitro-2₃-diamido-diphenyl (B. 25, 128).

o.p-Diamido-diphenyl, Diphenyline, melts at 45° and boils at 362°. Preparation, see henzidine (A. 207, 348; B. 22, 3011). o,p,-Triamido-diphenyl, m-Amidobenzidine, (B. 23, 797). 02,12. Tetramido-diphenyl, m2-diamidobensidine, melting at 1650, is obtained from o, dinitro-p,-diamido-diphenyl (see benzidine), and by loss of ammonia becomes p₂-diamido-carbazole.

Di-p-phenylenediamine, (NH₂), [2,5]C₆H₃. C₆H₈[2,5](NH₂), melting at 168°, is converted by hydrochloric acid at 180° into 5₂-diamido-carbazole (B. 25, 131).

Benzidine Homologues, p₂-Diamidophenyl-tolyl, o-Methyl Benzidine, H₂N. C₆-H4. (4H3(CH3). NH3, is formed upon reducing a mixture of nitrobenzene and o-nitrotoluene. It melts at 90° (B. 23, 3222).

o Tolidine, p. Diamido-m. dimethyldiphenyl, from o hydrazotoluene, melts at 1280

(B. 20, 2017; 23, 3252).

m. Tolidine, p. Diamido o dimethyldiphenyl, from m-hydrazotoluene (p. 117), melts at 100°. Isomeric ditolylin (B. 23, 3252) is produced at the same time.

o and m-Hydrazotoluenes suffer under the influence of acids the benzidine rearrange ment. p-Hydrazotoluene under like conditions follows the semidine rearrangement (p. 118).

Benzidine Dyes .- Benzidine yields azo dyes, transposition products of the diagochloride from benzidine and amidosulphonic acids, phenol carboxylic acids, and phenolsulphonic acids, which unite directly with cotton fiber (Griess, B. 22, 2469). These dyes are obtained as sodium salts, which are prepared by adding the aqueous solution of the tetrazochloride to the aqueous solution of two molecules of the sodium salt of the other component.

Sodium acetate, sodium carbonate, or ammonia is added to the solution of the sodium salt to combine the hydrochloric acid which is liberated:

$$\frac{c_{6} u_{4} N_{2}, c_{1}}{c_{6} u_{4} N_{2}, c_{1}} + \frac{c_{6} u_{4}(ou) co_{3} N_{a}}{c_{6} u_{4}(ou) co_{2} N_{a}} + co_{3} N_{a_{3}} = \frac{c_{6} u_{4} N_{1}, N, c_{6} u_{3}(ou) co_{3} N_{a}}{c_{6} u_{4} N_{1}, N, c_{6} u_{3}(ou), co_{3} N_{a}} + 2uc_{1} + co_{2} + u_{4} \alpha$$

The sodium salts of two different components can be, step by step, brought into reaction with the tetrazochloride, and mixed tetrazo dyes (B. 19, 1697, 1755; 20, R.273; 21, R. 71) result.

Representatives of the class of benzidine dyes are:

C6H4. N: N. C6H3(OH). CO2Na Chrysamine, Flavophenine, (6H₄. N:N. C₆H₃(OII). CO₂Na, which is made from diphenyltetrazochloride and sodium salicylate (equation above) (B. 22, 2459).

C₆H₄. N: N . C₈H₃(NH₂) . SO₃Na , is obtained from diphenyl tetra-Congo Yellow, (H4. N:N. C6H4. OH zochloride, phenol, and sulphanilic acid.

The preceding dyes color cotton fiber yellow.

The first red dye brought into commerce was Congo red, which is formed from the interaction of diphenyltetrazochloride and sodium naphthionate. It will be brought forward again under the naphthalene azo-dyes. The β -naphthylamine sulphonic acids are particularly valuable in the preparation of substantive dyes.

Substantive dyes, similar to those from benzidine, have been obtained from p, amidomethyldiphenyl, o-methylbenzidine, o- and m-tolidines, dianisidine (p. 337), thiobenzidine, thiotolidine (B. 20, R. 272), py-diamido-benzophenone (p. 347), py-diamido-stilbene

(p. 370) (B. 21, R. 383).

It may be said that, as a rule, those substituted benzidines (nitro and sulphobenzidines, tolidines, etc.) having the substituent in the meta-position (relative to the amido group) yield inactive or feeble substantive azo-dyes. Diamido-diphenylene oxide, benzidine sulphone (see this), and diamido carbazole (see this) constitute exceptions. They contain a third ring shaped chain (B. 23, 3252, 3268; 24, 1958).

It is interesting to observe that benzidine hydrochloride itself unites with cotton. It mordants the cotton. Hence it is possible to produce the benzidine upon the fiber (B. 19,

2014). The "one-sided diazotizing" of benzidine is attained through the action of a p-tetrazodiphenyl salt upon the aqueous solution of a benzidine salt (B. 27, 2627); compare migrations of the diazo-group, p. 100. When the bisdiazocompound of benzidine is al-

formazylcarboxylic Ester, $COOC_2H_5$ $N:NH-C_6H_4$ $N:N-C_6H_4$ a reddish-brown powder, fusing with difficulty (see formazyl carboxylic acid, p. 130); and with two molecules of

the ester:

Bisacetylglyoxylic Ester Phenylhydrazone, $[CH_2COC(CO_2C_2H_5): NNHC_4H_4-]_2$,

yellow needles, melting at 198° (A. 295, 332).
p-Hydrazinodiphenyl, C₆H₆C₆H₄[4]NH. NH₂ (B. 27, 3105).
Biphenylsulphonic Acids.—On digesting biphenyl with sulphuric acid the first product is biphenyl-p-sulphonic acid (its chloride melting at 115° and its amide at 115° and its chloride melting at 115° and its chloride melting at 115° and its chloride acid and its chloride at 115° and its chloride acid. 229°), and later biphenyl-p_s-disulphonic acid, melting at 72°, and its *chloride* at 203° (B. 13, 288). When potassium biphenyl-p-sulphonate is heated it changes to biphenyl and potassium biphenyl-p_s-disulphonate. Biphenyl-o_s-disulphonic Acid is obtained from benzidine-o_s-disulphonic acid (A. 261, 310).

Benzidine Sulphonic Acids: 42-Diamido-biphenyl-2, disulphonic Acid is formed from m-hydrazobenzene sulphonic acid (A. 261, 310; 268, 130), and when fused with caustic potash yields 4, diamido-diphenylene oxide.

42-Diamido-biphenyl-32-disulphonic Acid is produced on heating benzidine with

ordinary sulphuric acid to 210° (B. 22, 2466).
o-Tolidine Disulphonic Acid, 42 Diamido-53 dimethylbiphenyl-22 disulphonic Acid (A. 270, 359).

4₂-Dihydrazino-biphenyl-2₂-disulphonic Acid, $(C_6H_3 < \frac{N_2H_3}{SO_3H})$. See A. 261, 323. Ozybiphenyls are obtained from the biphenyl derivatives by methods similar to

those by which the phenols themselves are prepared from the benzene derivatives, and also in the oxidation of phenols containing a single nucleus, when they are fused with caustic potash (B. 27, 2107).

Monoxybiphenyls.—p-Oxybiphenyl, CaH5. CaH4[4]OH, melting at 165° and boiling

at 306°, is obtained from diazobenzene chloride and phenol (B. 23, 3708).

Dioxybiphenyls.—0, Dioxybiphenyl, o, Biphenol, melting at 98°, is made on fusing fluorene (see this) with caustic potash at 400°, and from biphenyl-o₃-disulphonic acid (A. **261**, 362). m-Biphenol, melting at 123.5°, is obtained from o-dianisidine and m₂-diamidobiphenyl (B. 27, 2107). p₂-Biphenol, melting at 272°, is prepared from benzidine, biphenyl-p₃-disulphonic acid, and from phenol by the action of KMnO₄ (B. 25, 200). Representations of the control of the con

R. 335). o,p-Biphenol, from diphenyline, melts at 160°.

Tetraoxybiphenyls.—Bipyrocatechine, (HO)₂C₆H₃. C₆H₃(OII)₃, melting at 84°,

Biresorcinol, melting at 310°, and bihydroquinone, melting at 237°, result when the three dioxybenzenes are fused with sodium hydroxide (B. 11, 1336; 12, 503; 18, R.

23).

Hexaoxybiphenyls.—Hydrocoerulignone is a derivative of hexaoxybiphenyl. Coerulignone, or cedriret, bears the same relation to it as quinone to hydroquinone.

Coerulignone, O₂: C₁₂H₆(OCH₃)₄, separates as a violet powder when crude woodspirit is purified on a large scale by means of potassium chromate. It is further formed on oxidizing dimethyl-pyrogallol (p. 164) with potassium chromate or ferric chloride:

$${}_{2}C_{6}H_{3}\underbrace{\{(O\cdot CH_{3})_{2}}_{OH} \xrightarrow{-_{4}H} \underbrace{(CH_{3}O)_{2}\colon C_{6}H_{2}O}_{(CH_{3}O)_{2}\colon C_{6}H_{3}O}$$

Coeruligone is insoluble in the ordinary solvents, and is precipitated in fine, steel-blue needles, from its phenol solution, by alcohol or ether. It dissolves in concentrated sulphuric acid with a beautiful blue color. Large quantities of water color the solution red at first. Reducing agents (tin and hydrochloric acid) convert coerulignone into colorless hydrocoerulignone, which changes again to the first by oxidation. Coerulignone is, therefore, a quinone body, and may be called a double-nuclei quinone.

It unites with primary aromatic amines, forming blue dyes. It is very probable that

in doing this two methoxyl groups are replaced by amino-residues (B. 30, 235).

Hydrocoerulignone, C₁₆H₁₈O₆, melts at 190°, and distils with almost no decompo-

When heated with concentrated hydrochloric acid it breaks down into methyl

chloride and Hexaoxydiphenyl, $C_{12}H_{10}O_{6}$ (B. 11, 797).

Amido-oxybiphenyls are obtained from oxybiphenyls (B. 22, 335), and from the alkyl ethers of oxyazoderivatives, having free p-positions, by the benzidine rearrangement (B. 23, 3256). In the coal-tar industry o-diamisidine or 42-diamido-32-dimethoxybiphenyl and ethoxybenzidine, from o-nitroanisol, are of great value. They yield violet, blue, and black substantive cotton dyes with amidonaphtbalene sulphonic acid, naphthol sulphonic acid, and amid naphthol sulphonic acids: azoviolet, benzasarine, diamine black, etc. (B. 22, R. 372; 24, R. 55, 56, etc.).

Biphenyl Carboxylic Acids are obtained from diphenyl derivatives by reactions

similar to those by which the benzene carboxylic acids are prepared from the derivatives of benzene. They are of just as much importance in determining the constitution of

diphenyl bodies as the benzene-carboxylic acids for the benzene compounds.

Biphenyl Monocarboxylic Acids.—There are three possible acids: o-Phenyl-benzoic Acid, C_6H_5 , $C_6H_6[2]CO_3H$, melting at 111°, is produced by fusing diphenylene ketone with caustic potash (A. 166, 374); by the distillation of sodium salicylate with triphenyl phosphate (J. pr. Ch. [2], 28, 305); and from o-amido- and o-methyl-diphenyl. If the acid be treated with PCl₅, or if it be heated with sulphuric acid to 100°, or with lime to more elevated temperatures, diphenylene ketone will be formed (A. 266, 142; 279, 259). m-Phenyl-benzoic Acid, melting at 160°, results from the oxidation of m methylbiphenyl, of isodiphenylbenzene (see this), and in the reduction of bromm-phenylbenzoic acid (B. 27, 3390).

p Phenyl-benzoic Acid, melting at 218°, is obtained from p-methylbiphenyl, from p diphenylbenzene, from sodium biphenylsulphonate (A. 282, 143), from p-amidodiphenyl, and by fusing benzoic acid with caustic potash. It is reduced to p-phenylhexahydro-benzoic acid, C₆H₁₀[4]CO₃H, melting at 202°, which upon heating to 100° with hydrochloric acid is rearranged to phenylisoherahydrobenzoic acid, melting at 113° (A. 282, 130). p. Nitrophenylbenzoic Acid, melting at 222-225°, results from the oxidation of p₂ nitrophenyl tolyl. It yields the corresponding amido-acid (B. 29, 166) on reduction.

Oxybiphenyl Carboxylic Acids.—The following acids are all derivatives of o phenylbenzoic acid.

6. Phenyl-salicylic Acid, C₆II₅[6]C₆II₃[2](OH)CO₂II, melting at 159°, results

upon fusing 3-oxydiphenylene ketone and potassium hydroxide (B. 28, 112).

2 Phenyl m-oxybenzoic Acid, C₆H₅[2]C₆H₃[3]OH, CO₂H, melting at 154°, is obtained, together with [biphenylmethylo.id], as the principal product in the fusion of 6oxydiphenylene ketone with potassium hydroxide (A. 284, 307).

o Oxyphenyl o benzoic Acid is only known in the form of its lactone, [biphenyl-

methylolid], $\begin{array}{c} C_6H_4[2]CO \\ C_6H_4[2]O \end{array}$, melting at 92.5°, which is formed as a by-product on fusing 6oxydiphenylene ketone or o oxyfluorenone with caustic potash, in small quantities by the action of POCl3 upon sodium salicylate, and when phenol acts upon the sulphate of o-diazobenzene (A. 284, 316). It corresponds in composition to phenanthridone, 1, melting at 293° (see this), which is produced when bromine and caustic C₆H₄[2]NH

potash act upon diphenamic acid (A. 276, 245).

o-Oxyphenyl-o-benzoic Acid, HO[4]C₆H₄[1]C₆H₄[2]CO₂H, melting at 206°, is produced, together with [biphenylmethylolid] and phenyl-ether salicylic acid, by the action of phenol upon the sulphate of o-diazobenzoic acid (A. 286, 323).

Biphenyl Dicarboxylic Acids contain the two CO2H-groups, either linked to the same or to different benzene residues. Diphenic acid is the most important biphenyl

dicarboxylic acid.

[5] Phenylisophthalic Acid, $C_6H_6[5]C_6H_3[1,3](CO_2H_2)$, melts above 310°, and is formed on boiling benzaldehyde and pyroracemic acid with baryta-water (B. 24. 1750).

Diphenic Acid, o₂ Biphenyldicarboxylic Acid, CO₂H[2]C₆H₄. C₆H₄[2]CO₂H, melts at 229°. It is produced in the oxidation of phenanthraquinone with a chromic acid mixture, or by boiling it with alcoholic potash. The constitution of phenanthrene

follows from its constitution. That of diphenic acid (2) is evident from its oxidation to o-phthalic acid (1) (Anschütz and Japp, B. 11, 211) by potassium permanganate, and its formation by the deamidation of padiamido-diphenyl-oa-dicarboxylic acid (3), which is obtained on the one hand from p₃-dinitrodiphenic acid (4), and on the other by the rearrangement of m-hydrazobenzoic acid (5) (G. Schultz, A. 204, 95):

In this circle of reactions there should also be included the formation of pg-dinitrodiphenic acid by the oxidation of p. dinitrophenanthraquinone (6) and the transposition of diamidodiphenic acid to benzidine (7), the constitution of which was previously deduced (p. 337), and to p₂-diamido-fluorene (8).

Concentrated sulphuric acid changes diphenic acid to diphenylene ketone carboxylic acid (see this). When it is digested with acetyl chloride or acetic anhydride it yields Diphenic Anhydride, C₆H₄. CO O, melting at 213° (A. 226, I). This is a remarkable compound, inasmuch as it can be viewed as adipic anhydride and contains a C₆H₄ . COCl "seven-membered" ring. Diphenic Chloride, $C_{g}II_{4}$. COCl, melting at 93°, is re duced in ethereal solution by zinc and hydrochloric acid to phenanthrene hydroquinone, Diphenamino-acid, C₆H₄. CO. OH, melting at 193°, C_4H_4 . C(OH)(A. 247, 268). C.H. . C(OH) is converted by a hypobromite or hypochlorite, in alkaline solution, into phenanthridone Diphenimide, C₆H₄. CO NH, melts at 219° (A. 247, 271). (see this) (A. 276, 248).

NO₂[4]C₆H₃[2]CO₂H melts at 253°. See diphenic acid NO₄[4]C₆H₃[2]CO₂H, p. Dinitrodiphenic Acid, for its formation.

p₃-Diamidodiphenic Acid—for its formation and decomposition see diphenic acid. Isodiphenic Acid (0,m') CO₂H[3]C₆H₄. C₆H₄[2]CO₂H, melting at 216°, is produced when diphenyleneketone carboxylic acid (see this) is fused with caustic potash. o,p'.Biphenyldicarboxylic Acid, CO₂H[4]C₆H₄. C₆H₄[2]CO₂H, melting at 251°, is obtained from diphenyline (p. 338) (B. 22, 3019).

p. Biphenyldicarboxylic Acid decomposes at a more elevated temperature. It is

obtained from diphenyl-p₂-dicyanide and by oxidizing p₂-ditolyl.
p₃-Diamidobiphenyl-m₂-dicarboxylic Acid is obtained from o-nitrobenzoic acid, just as p.-diamidodiphenic acid is prepared from m-nitrobenzoic acid (B. 25, 2797).

m₂. Dimethyl-biphenyl-p₂-dicarboxylic Acid melts above 300°, is formed from o-tolidine (p. 338) and is oxidized to diphthalic acid, biphenyl-m₂,p₂-dicarboxylic acid,

(CO₃H)₂[3,4]C₆H₃. C₆H₃[3,4](CO₂H)₃ (B. 26, 2486).

I B. Diphenylbenzenes, Diphenylphenylenes, C₆H₄(C₆H₅)₃.—Two such bodies are known: m Diphenylbenzene, Isodiphenylbenzene, melting at 85° and boiling at 369°, and p Diphenylbenzene, melting at 205° and boiling at 383°. They are formed simultaneously on conducting benzene through a tube heated to redness, and by the action of diazobenzene chloride upon diphenyl and Al₂Cl₆ (B. 26, 1998). The p-body is also produced in the action of sodium upon a mixture of p-dibrombenzene and brombenzene

(A. 164, 168). Isodiphenylbenzene is also prepared from m-dichlorbenzene and chlorbenzene by the action of sodium in xylene (B. 29, R. 773).

I.C. Triphenyl Benzenes, C₈H₂(C₈H₈).—The symmetrical or [x,3,5] modification is formed from acetophenone when heated with P₂O₈, or by conducting hydrochloric forms. acid gas into it, just as mesitylene is obtained from acetone (p. 214). It melts at 169° (B. 23, 2533). [1,2,3] (?) Triphenyl Benzene melts at 157° (B. 26, 69).

II. BENZYLBENZENE GROUP.

Benzylbenzene or diphenyl methane is the simplest hydrocarbon of this The alkyl diphenylmethanes, and the compounds substituted in the benzene residues by the NO2, NH2, or OH-groups, are derived from it. If we suppose an hydrogen atom of the CH₁-group to be replaced by OH, we obtain the formula of benzhydrol or diphenylcarbinol, which changes by oxidation to benzophenone or diphenylketone. Diphenylmethane, $(H_2(C_6H_5)_2$, benzhydrol, $HOCH(C_6H_5)_2$, and benzophenone, $CO(C_6H_5)_2$, are the simplest representatives of the hydrocarbons, the secondary alcohols and the ketones of this group. Attached to them are the corresponding carboxylic acids—e. g.:

1. HYDROCARBONS (DIPHENYL METHANES).

Formation.—(1) From benzyl chloride, benzene and zinc-dust (Zincke, A. 159, 374), or aluminium chloride (Friedel and Crafts). (2) From formaldehyde, methylal, or methylene diacetate with benzene and sulphuric acid (Baeyer, B. 6, 963). Both reactions are capable of wide generalization. Thus, by use of the second reaction, substituting other aldehydes for formaldehyde, numerous hydrocarbons have been obtained in which two benzene residues are attached to the same carbon atom (see unsymdiphenyl-ethane, p. 368).

Both reactions, upon substituting phenol ethers or dialkyl anilines for benzene, lead to RO- and R.N-substitution products.

(3) Aromatic alcohols condense with aromatic hydrocarbons to benzyl benzenes—e. g., benzyl alcohol and benzene yield diphenyl methane (B. **6,** 963).

(4) By the reduction of ketones, into which the benzyl benzenes are

oxidized.

Ì

Diphenyl Methane, C₆H₅. CH₂. C₆H₅, Benzyl Benzene, is obtained (1) from benzyl chloride and benzene with zinc-dust or AlCl₃; (2) from CH₂Cl₂ with benzene and AlCl₃; (3) from methylal, or (4) from benzyl alcohol, benzene, and sulphuric acid; (5) by the reduction of benzophenone with zinc-dust, or zinc and sulphuric acid, or hydriodic acid and phosphorus, and (6) upon distilling diphenylacetic acid (p. 368) with soda-lime (A. 155, 86).

Diphenyl methane possesses the odor of oranges. It melts at 26.5° and boils at 261°. When conducted through ignited tubes it yields diphenylene methane or fluorene; a chromic acid mixture oxidizes it to benzophenone, whereas concentrated nitric acid

changes it to p₂-, o,p-dinitro- and tetranitrodiphenylmethane (A. 283, 154).

Benzyl Toluenes, *Phenyl Tolyl Methanes*, C₆H₅. CH₂. C₆H₄. CH₃.—A liquid mixture of o- and p-benzyl toluene, which cannot be separated, is obtained by the action of zinc-dust on a mixture of benzyl chloride and toluene. Anthracene is formed at the same time. The pure para-body has been formed by heating para phenyl tolyl ketone with zinc-dust, and is a liquid, boiling at 285°. It appears also to be produced in the action of sodium upon p-bromtoluene along with p-ditolyl (p. 336). Brommesitylene and sodium yield, together with dimesityl, a pentamethyldiphenyl methane (B. 29, 111).

Benzyl-p-xylene boils at 294°. Benzyl Mesitylene melts at 36° and boils at 301°. The benzyl durenes melt at 60° and boil at 310°; and at 145° and 326°. Benzyl Pentaethyl Benzene melts at 88° (B. 26, R. 58). p.-Ditolylmethane melts at 22° and boils at 286°. Dimesityl Methane melts at 139°. The unsym. hydrocarbons were obtained according to methods I and 4, and the sym. according to method I.

Nitrodiphenyl Methanes, C₈H₅. CH₂. C₆H₄. NO₂ (A. 283, 157).—The orthocompound, prepared from o-nitrobenzyl chloride and benzene with AlCl₃, is liquid (B. 18, 2402; 29, 1303). The meta- and para-bodies are derived from meta- and para-nitrobenzyl alcohol by means of benzene and sulphuric acid. The first is an oil; the second

melts at 31° (B. 16, 2716).

m,-Dinitrodiphenyl Methane, melting at 174°, is formed from m-nitrobenzyl alcohol with nitrobenzene, or from formaldehyde, nitrobenzene and concentrated sulphuric acid (B. 27, 2293, 2321). m,p-Dinitrodiphenyl Methane, p-Nitrobenzyl-m-nitrobenzene, melts at 103°. p₃-Dinitrodiphenyl Methane melts at 183°. It is obtained from diphenyl methane along with o,p-dinitrodiphenyl methane, melting at 118° (B. 27, 2110; A. 194, 363).

Tetranitrodiphenyl Methane, melting at 172°, forms dark blue colored salts with

alcoholic potash (B. 21, 2475).

Amido-diphenyl Methanes.—o-Amido-diphenyl Methane is a liquid. vapors are conducted over ignited lead oxide, acridine (see this) results. Nitrous acid converts it into fluorene (B. 27, 2786). m- and p-Amido-diphenyl Methane melt at 46° and 34° respectively (B. 16, 2718).

p. Diamido-diphenyl Methane, melting at 85°, is also produced from methylene diphenylimide in the presence of hydrochloric acid or aniline hydrochloride by an intramolecular atomic displacement, which recalls the benzidine transposition and the formation of aniline homologues from the phenylalkylamines (p. 73). It changes completely to para-rosaniline or rosaniline when heated with aniline or o-toluidine in the presence of an oxidizing agent (B. 25, 303).

Its tetramethyl derivative results from dimethyl aniline by means of C₂H₂I₂, CCl₂II, (or CCla), or with methylal, or by the action of CS, and zinc upon dimethyl aniline. It

melts at 90°.

The hydrogen of the group CH, attached to basic radicals is very readily replaced by sulphur; see p₂-tetramethyl-diamidothiobenzophenone (p. 348). See A. 283, 149, for isomeric diamidodiphenyl methanes.

Oxybenzyl Benzenes.-p-Benzyl Phenol, melting at 84° and boiling at 325° (in CO,), is produced (1) from benzyl chloride, phenol, and zinc; (2) from benzyl alcohol, phenol with concentrated sulphuric acid, or zinc chloride; (3) from p-amido-diphenyl methane.

o₂-Dioxydiphenyl Methane is only known in the form of its anhydride, xanthene (see

this).

p₂-Dioxydiphenyl Methane is produced on fusing diphenyl methane disulphonic acid with KOH (A. 194, 318). It melts at 158°. Its dimethyl ether is formed from anisol and methylal by the action of concentrated sulphuric acid (B. 7, 1200), and melts

Methylene Dipyrocatechol, CH₂[C₆H₃(OH)₂]₃, melting with decomposition at 220°, is produced on boiling a solution of pyrocatechin and formaldehyde with hydro-

chloric acid or sulphuric acid (B. 26, 254).

2. ALCOHOLS (BENZHYDROLS).

Diphenyl Carbinol, Benzhydrol, $(C_0H_0)_2CH$. OH, melts at 68° and boils at 298° with partial decomposition into water and benzhydrol ether, $[(C_0H_0)_2.CH]_2O$, melting at 199°. It is produced on heating diphenyl brom-methane with water to 150°; more readily from benzophenone with sodium amalgam, or by heating with alcoholic potassium hydroxide and zinc-dust (together with benzpinacone) (A. 184, 174).

Phenyl-p-tolyl Carbinol melts at 52° (A. 194, 265).

Diphenyl Carbinol Chloride, *Diphenyl Chlormethane*, melting at 14°, is obtained from benzhydrol and IICl. When heated it breaks down into HCl and tetraphenyl ethylene (p. 378) (B. 7, 1128). Diphenylbrom-methane, from diphenylmethane and bromine, melts at 45°.

Benzhydrylamine, NII₂. CH(C₆H₅)₂, boiling at 288°, is obtained from diphenylbrommethane and from benzophenonoxime (B. 19, 3233). The latter method has afforded the homologous alkylbenzhydroxylamines (B. 24, 2797). The formyl derivative, from benzophenone and ammonium formate at 200-250° (B. 19, 2129), melts at 132°. The thionyl compound boils at 88° (35 mm.) (B. 26, 2189). Dibenzhydrylamine melts at 136°.

 β -Benzhydrylhydroxylamine, [Diphenylaminol Methane], HO.NH. CH(C_2H_1),

melting at 78°, is formed on boiling a solution of diphenyl brom-methane and acetoxime with glacial acetic acid and water (A. 278, 364).

o-Amidobenzhydrol, C₆H₄< CH(OH)C₆H₆, melting at 120°, is formed in the reduction of a amidobenzhydrol. duction of o-amidobenzophenone. It is capable, like o-amidobenzyl alcohol (p. 180), of producing heterocyclic compounds (B. 29, 1304).

In the aldol condensation of benzaldehyde or p-nitrobenzaldehyde and dimethyl aniline with hydrochloric acid (by ZnCl, or oxalic acid the products are triphenylmethane

derivatives) there arise:

p-Dimethyl Amidobenzhydrol, C₆H₅CH(OH). C₆H₄N(CH₃)₂, melting at 69°, and p-Dimethylamido-p-nitrobenzhydrol, melting at 96° (B. 21, 3292). By reduction the latter compound yields p-dimethyl-amido-p-amido-diphenylmethane, melting at 165°. p-Tetramethyl-diamido-benzhydrol, melting at 96°, has been obtained by the reduction of p₂-tetramethyldiamidobenzophenone (B. 22, 1879). On boiling the former with dilute mineral acids until the blue color has disappeared, it breaks down into dimethylaniline and dimethylamidobenzaldehyde (B. 27, 3316). In the solid condition p, tetramethyldiamidobenzhydrol is white, while its solution is blue in color (B. 20, 1733 Anm.).

3. KETONES (BENZOPHENONES).

The ketones of the benzylbenzene group bear the same relation to the benzoic acids that the acetones bear to the fatty acids:

This analogy is shown in the various methods of formation.

Methods of Formation.—(1) By oxidizing (a) the benzyl benzenes and (b) the benzhydrols with chromic acid:

$$CH_{1} < \begin{matrix} C_{6}H_{5} & 2O \\ C_{6}H_{5} & -2O \end{matrix} \rightarrow CO < \begin{matrix} C_{6}H_{5} \\ C_{6}H_{5} & -O \end{matrix} - HOCH < \begin{matrix} C_{6}H_{5} \\ C_{6}H_{5} & -O \end{matrix}$$

If the CH₂-group contains alkyls or carboxyl, these groups will be split off by the oxidation, with the production of ketones. If the benzene residues contain alkyl groups these are converted into carboxyl groups.

(2) By the action of hot water upon the ketone chlorides (see benzo-

phenone chloride, below).

Nucleus Syntheses. -(3) By the distillation of the calcium salts of mononucleus, aromatic monocarboxylic acids, the CO₂H-groups of which are in direct union with the benzene residue:

$$\begin{array}{c} C_{\mathbf{c}}H_{\mathbf{5}} \cdot \begin{array}{c} COO \\ C_{\mathbf{c}}H_{\mathbf{5}} \cdot \begin{array}{c} COO \\ C_{\mathbf{c}}H_{\mathbf{5}} \end{array} \\ \end{array} > CO + CO_{\mathbf{5}}Ca.$$

(4) By the condensation of benzoic acid or its anhydride on heating with benzene and

(5) By the action of benzoyl chloride on benzene, in the presence of aluminium chloride.

Phosgene reacts in the same manner, and acid chlorides are the first products. These then change into ketones (B. 10, 1854):

$$COCl_2 + C_6H_6 \xrightarrow{-HCl} C_6H_5 \cdot COCl + C_6H_6 \xrightarrow{-HCl} C_6H_6COC_6H_6.$$

(6) By the action of mercury diphenyl upon the acid chlorides—e. g., benzoyl chloride.

Behavior.—(1) On heating with zinc-dust or hydriodic acid and amorphous phosphorus, the ketones sustain a reduction of the CO group and revert to the hydrocarbons; for example, diphenyl ketone yields diphenyl (2) Sodium amalgam changes them to secondary alcohols methane.

(benzhydrols) and pinacones.

Benzophenone, Diphenyl Ketone, CO(C₆H₅)₂, is known in two modifications, the unstable (labile), melting at 26°, and produced on boiling the stable form, melting at 46°. The unstable modification slowly reverts to the more stable variety. This takes place rapidly, and with a very perceptible evolution of heat, upon touching it with a trace of the stable variety (B. 26, R. 380). Benzophenone has an aromatic odor. It boils at 307° (760 mm.) and at 162° (12 mm.). It is produced according to the general methods: (1) by oxidizing diphenyl methane, unsymmetrical diphenyl ethane (p. 368), benzhydrol, diphenylacetic acid (p. 368), etc.; (2) from benzophenone chloride; (3) by the distillation of calcium benzoate; (4) by the action of P2O6 upon benzoic acid and benzene; (5) from phosgene or benzoyl chloride, benzene and aluminium chloride, and (6) from benzoyl chloride and mercury diphenyl. When fused with caustic potash it breaks down into benzoic acid and benzene. It is converted into diphenylmethane, benzhydrol, and benzpinacone by reduction (p. 378).

Benzophenone Homologues. - o-Phenyltolyl Ketone, boiling at 315°, when conducted

over heated lead oxide, passes into anthraquinone (see this), while it yields anthracene when heated with zinc-dust (B. 6, 754). m-Phenyltolyl Ketone boils at 314°. p-Tolylphenyl Ketone is known in two modifications: the unstable (labile) form sets at 55°; it is hexagonal. The stable form, melting at 59°, is monoclinic (A. 189,

&; B. 12, 2299).

p. Ditolyl Ketone melts at 92° and boils at 333°. Benzoyl Xylene melts at 36° and boils at 317° (B. 17, 2847). Benzoyl Mesitylene melts at 36° and boils at 317° (J. pr. Ch. [2], 35, 486), etc. All these are most conveniently prepared by method 5. Derivatives of Benzophenone Obtained by the Replacement of Oxygen.—Benzophenone Chloride, Diphenyldichlormethane, CCl₂(C₆H₅)₂, boiling at 193° (30 mm.),

is produced when PCl_5 acts upon benzophenone. When heated with water it rebenzophenone, while with silver it yields tetraphenylethylene (p. 378), and wit dust tetraphenylethylene, a- and β -benzpinacoline (B. 29, 1790). Benzopt Bromide, $CBr_3(C_6ll_5)_2$, is produced on dropping bromine into diphenylmethane to 150°.

Actuals of benzophenone are obtained from benzophenone chloride with sodius holates, as well as from benzophenone and otho-formic ethers (see p. 189). Dimes and diethoxydiphenyl methane melt at 107° and 52°, and boil at 289° and 2000 at 280° at

29, 2932; R. 774).

Thiobenzophenone, CS(C₆H₅)₃, is derived from benzene by means of thiophi CS₄Cl₂, and aluminium chloride. In this reaction the phenol ethers react more than the hydrocarlons (B. 28, 2869). Thiobenzophenone is further produced action of phosphorus sulphide upon benzophenone, but best of all when an assolution of potassium sulphide reacts with benzophenone chloride. It is an intensel colored oil, which congeals at lower temperatures to blue needles, and under a p of 14 mm. distils at 174°. The thiobenzophenones, when acted upon with n copper, yield tetraphenylethylene and its substitution products (B. 29, 2944).

Diphenyldinitromethane, $(C_6H_5)_2C(N_2O_4)$, melting at 78°, results upon sat a solution of benzophenone-oxime in ether with nitrogen tetroxide. It is changed to benzophenone-oxime with zinc-dust and glacial acetic acid. Benzhydrylamine formed (B. 23, 3490).

Imidobenzophenone, $(C_6H_5)_2C = NH$, is a colorless oil, obtained in the act dry ammonia upon a chloroform solution of amido-benzophenone chlorhydrate. chlorhydrate results when benzophenone chloride is heated with urethane to 130°. water readily decomposes it into benzophenone and ammonium chloride. Pheny

zalsultime, C_6H_4 $C(C_6H_5)$ N, melting at 164°, should be viewed as a derival imidobenzophenone, produced in the condensation of pseudosaccharin chloride (I with benzene and aluminium chloride (B. 29, 2296).

Phenylimidobenzophenone, Diphenylmethylene Aniline, $(C_6H_6)_1C=N$. melting at 109°, is formed from benzophenone chloride and aniline (A. 187, 199).

Benzophenonoxime, (C₆H₅)₂C: N. OH, melting at 140°, is known in onl modification (for the possible existence of an unstable (labile) form consult B.: 1008), while unsymmetrical benzophenones—e. g., brombenzophenone and pheny ketone—each form two oximes (B. 23, 2776). It is also formed in the interaction o benzophenone and hydroxylamine.

Benzophenoxime, when digested at 100° with sulphuric acid, with hydrochlori and glacial acetic acid, etc., sustains a peculiar molecular rearrangement into be ilide. The isomeric benzanilide imide-chloride is produced in like manner from imide chloride formed by PCl₆ (p. 199) (B. 22, R. 591). The phenylhydrazone, (CC: N₂H. C₆H₅, melts at 137° (B. 19, R. 302).

Benzophenone Ilalogen Derivatives are mostly produced by method 5 (p. o-Brombenzophenone, melting at 42°, is noteworthy because of the mobility bromine atom. If o-brombenzophenone oxime, melting at 132°, be acted upor caustic alkali it splits off hydrogen bromide and becomes phenylindoxazene,

 C_6H_4 C N (see this) (B. 27, 1452), while m- and p-brombenzophenone, on the

hand, yield with o-brombenzophenone two isomeric oximes (B. 25, 3293; A. 264,

The sym. m-, p-Dibrombenzophenones, (BrC₆H₄)₂CO, melting at 142° and yield but one oxime (A. 264, 160). o,p-Dibrombenzophenone, melting at yields one oxime, melting at 141°; this can be readily rearranged to p-bromph indoxazene (B. 27, 1453).

o-Chlorbenzophenone Oxime shows less readily and o-iodbenzophenone o more readily than o-brombenzophenone oxime the formation of phenylindoxazene (E 1250).

Nitrobensophenones.—o-, m-, and p-Nitrobenzophenone melt at 195°, 94°, and 138° (B. 16, 2717; 18, 2401). Phenylindoxazene is produced when the oxime of the o-body is boiled with caustic soda (B. 26, 1250). o_2 -, m_2 -, p_2 -Dinitrobenzophenone melt at 188° (γ), 148° (β), and 189° (a). o,m-, o,p-, m,p-Dinitrobenzophenone, (NO₂C₂H₄)₂CO, melt at 126° (ϵ), 196° (δ), and 172°. o_2 - and o,m-Dinitrobenzophenones are formed in the nitration of benzophenone (A. 283, 164; B. 27, 2111). o_2 , p_2 -Tetranitrobenzophenone melts at 225° (B. 27, 2318). Other substituted benzophenones are described in the A. 286, 306, etc.

Amidobenzophenones are obtained from nitrobenzophenones, from benzoic acid, dimethyl aniline and P₂O₅, benzoyl chloride, phthalanil and ZnCl₂ (B. 14, 1838), etc. p-, m-, p-Amidobenzophenone melt at 106°, 87°, and 124°. o-Amidobenzophenone is made from the amide of o-benzoyl benzoic acid by the action of sodium hypobromite (B. 27, 3483; A. 291, 8). o-Amidobenzophenone Oxime, melting at 156°, is rearranged at high temperatures by hydrochloric acid into phenyl benzimide azole or o-phenylenebenzamidine (B. 24, 2385). Acetyl o-amidobenzophenone melts at 89°. p-Dimethylamidobenzophenone, p-Benzoyldimethyl Aniline, melting at 90°, is also formed on heating malachite green with concentrated hydrochloric acid at 180° (A. 217,

257; B. 21, 3293).

Ring-formations of o-Amidobenzophenone.—(1) Acridone is produced when o-amidobenzophenone is heated with lead oxide (B. 27, 3484). (2) Nitrous acid converts this o-body into fluorenone or diphenylene ketone (B. 27, 3484). (3) a-Phenylindoxacene is readily obtained from o-amidobenzophenone and nitrous acid (B. 26, 1667). (4) When acetyl-o-amidobenzophenone is heated with alcoholic ammonia it condenses to phen- β -methyl-a-phenylmiazine or a-phenyl- β -methyl quinazoline (B. 25, 3082). (5) Acetyl-phenylsindasole (B. 24, 2383; 29, 1255) results when acetyl-o-amidobenzophenone oxime is rearranged by contact with Beckmann's mixture. (6) o-Amidobenzophenone condenses with acetone and sodium hydroxide to a methyl-3-phenylquinoline (B. 18, 2405). (7) When heated to 200° with cyanacetic ester the product is β -cyan-y-phenylpseudocarbostyril (B. 27, R. 589). (8) With urea it yields 4-phenylquinazolon (B. 29, 1310). (9) When the hydrochloride of o-amidobenzophenone is heated water is eliminated and there results an anhydro-bis-o-amidobenzophenone, which probably contains an "8-membered" ring (B. 29, 1272):

Diamidobenzophenones.—o₂-, m_q-, p₂-Diamidobenzophenones melt at 134°, 173°, and 239°. Nitrous acid converts the o-body into xanthone (see this) and o-oxystomose (B. 28, 111). p₂-Diamidobenzophenone yields substantive cotton dyes (B. 22, 988).

Tetramethyl-p₂-diamidobenzophenone, CO< $^{C_8H_4}_{C_6H_4}$. $\stackrel{N(CH_2)_2}{N(CH_3)_2}$, results upon hesting hexamethyl violet with hydrochloric acid (B. 19, 109). It is technically prepared by the action of COCl, upon dimethyl aniline in the presence of AlCla. It melts at 173°. Nitrous acid converts it into nitrosotrimethyldiamidobenzophenone (B. 24, 3198).

with phenylnaphthylamine. Its oxime melts at 233° (B. 19, 1852). Its kydratone melts at 174° (13. 20, 1112)

Tetramethyl p. diamido-thiobenzophenone, CS[C4H4. N(CH3)2]2, results from the action of hydrogen sulphide upon an alcoholic auramine solution heated to 60°, or it can be prepared from dimethylaniline and CSCl2. It consists of ruby red crystalline leafets with a blue lustre or a cantharides-green crystalline powder, melting at 202° (B. 20, 3266, 3290).

Dimethylaniline and PCl, convert it into methyl violet, while it yields l'atoria blu

Auramine, Tetramethyl-pg-diamide-imidobencophenone Hydrochloride,

Auramine, Tetramethyt-p₂-diamias-imiasoem: apaenone Hydrocktoride,
$$Cl(CH_3)_2N = C_0H_4$$
 $C.NH_2$ (B. 26, R. 406), $(CH_3)_2N = C_0H_4$ $C.NH_2$ (B. 26, R. 406),

results when tetramethyldiamidobenzophenone is heated with ammonium chloride and zinc chloride, as well as from p-dimethylamidobenzamide by the action of dimethylanline and zinc chloride (B. 28, R. 86). Perfectly analagous dyestuffs are obtained from the primary anilines and diamines (B. 20, 2844; 28, R. 65). Auramine, golden-yellor leaflets, is important as a cotton dye. Cotton mordanted with tannin is colored a beamful yellow by this salt.

Potassium cyanide changes it to the nitrile of the corresponding tetramethyldiamide

diphenylacetic acid (B. 27, 3294).
(1)0,m-, (1)0,p-, (5)m,p-Diamidobenzophenones melt at 80°, 128°, and 126° (A.

283, 149; B. 28, 111).

Oxybenzophenones are formed: (1) From amidobenzophenones; in this change the o amidoben ophenones (p. 347) pass chiefly into fluorenones. (2) By decomposing the anthones, which may be viewed as cyclic phenyl ethers of o-dioxybenzophenones, with caustic potash. (3) By the condensation of benzoic acids or oxybenzoic acids and phenols with zinc chloride or phosphorus oxychloride (B. 26, R. 587), sulphuric acid or tin tetrachloride (B. 23, R. 43, 188; 24, 967). (4) From phenols by means of benzoyl chloride, zinc dust, or zinc chloride, or aluminium chloride (B. 12, 261). (5) By the action of benzotrichloride and zinc oxide (B. 10, 1969) upon phenols or their benzotl esters. (6) By the action of alkalies upon benzotrichloride and phenols (B. 24, 3677).

Oxyhensophenones containing but one hydroxyl-group in one benzene residue. -- Oxybenzophenone, o Benzoylphenol, melting at 41°, is produced, together with the phenyl ester of benzoic acid, by the 6th method of formation; also from phenylindoxazone (see this) upon heating it with hydriodic acid and phosphorus (B. 29, R. 350). The best method, however, consists in treating methyl salicylic chloride with benzene and aluminium chloride (B. 29, 824). m-Oxybenzophenone, melting at 116°, is produced according to method I (B. 24, 4044). p-Oxybenzophenone, melting at 134°, is produced by methods I, 4, and 5 (B. 25, 3533). (γ) α_2 -, (β) α_2 -, (α) α_2 -, (α) α_2 -, (α) α_3 -, (α) α_4 -, (α) α_5 phenones.

oz-Dioxybenzophenone is also made from its anhydride, xanthone or diphenylene ketone oxide, by careful fusion with potassium hydrate (B. 19, 2609). o.p. and p. Dioxybenzophenones are also produced in the condensation of salicylic acid and phenol with tin tetrachloride (A. 283, 175). p₂-Dioxybenzophenone appears also in the decomposition of aurine, benzaurine, phenolphthalein, and rosaniline upon heating them with

water or caustic potash (B. 16, 1931).

Oxybenzophenones containing more than one hydroxyl attached to one Benzene-nucleus.—These are prepared mainly by method 3 (p. 345). Mention must be made of the ketones obtained from pyrogallic acid and gallic acid, for they, like alizarine, are dyes. The dyestuff prepared from benzoic acid and pyrogallol melts at 140°. It bears the

Benzoyl-2.5-dioxybenzene, C₆H₅COC₆H₃[2,5](OH)₂, melting at 125°, is obtained from benzaldehyde and quinone, exposed to sunlight (B. 24, 1340; p. 167).

The barks of coto and paracoto, found in Bolivia, and possessing therapeutic value, contain a series of benzophenone derivatives. They are:

Cotoin, C₈H₅. CO. C₆H₁(OH)₂(OCH₃), melting at 130°;

Hydrocotoin, C₈H₅. CO. C₆H₁(OH) (OCH₃)₁, melting at 98°;

Methyl Hydrocotoin, C₈H₅. CO. C₆H₃(OCH₃)₃, melting at 113° (B. 25, 1119;

26, 2340; 27, 419), which are methyl ethers of benzoyl phloroglucin; and Protocotoin, (CH₃O)₂(HO). C₆H₂. CO. C₆H₃(O₂CH₃), melting at 141°, as well as Methyl Protocotoin, (CH₃O)₃. C₆H₃. CO. C₆H₃(O₂CH₃), melting at 134°, derivatives of 1,3,5-trioxybenzoprotocatechone.

4. CARBOXYLIC ACIDS OF THE DIPHENYLMETHANE GROUP.

There are three classes of these acids: A. Diphenylmethane Carboxylic Acids; B.

Benzhydrol Carboxylic Acids; C. Benzophenone Carboxylic Acids.

A. Diphenylmethane Carboxylic Acids.—o., m., p. Benzyl-benzoic Acids, C. H₅.—CH₄. C. L. CO₂H, melt at 117°, 107°, and 154°. When the o-acid is digested with sulphuric acid, anthranol (see this) is produced (B. 25, 3022; 27, 2789; A. 291, 17) (B. 9, 633). o-Cyandiphenyl Methane, melting at 19° and boiling at 313°, is obfained from o-cyanbenzyl chloride by means of benzene and aluminium chloride, as well s from o-amidodiphenylmethane.

Benzyliso- and -terephthalic Acid, C₆H₆. CH₂. C₆H₃(CO₂H)—see B. 9, 1765. Diphenylmethane o₂-dicarboxylic Acid, CH₂(C₆H₄[2]CO₂H)₂, melting at 254°, results from the reduction of the lactone of benzhydrol-o₂-dicarboxylic acid, and that of the dilactone of benzophenone-o. dicarboxylic acid. Concentrated sulphuric acid changes it to anthranolcarboxylic acid (A. 242, 253).

Diphenylmethane-m, dicarboxylic Acid melts at 220-225°. Diphenylmethanep-dicarboxylic Acid melts at 290° (B. 27, 2324).

B. Benzhydrol Carboxylic Acids. - o-Benzhydrylbenzoic Acid Lactone, Phenylphthalide, C_6H_6 [1]CH $-C_6H_5$ [2]COO , melting at 115°, is formed by the reduction of o-ben-

zoyl benzoic acid, and by the breaking down of benzhydrol-og-carboxylic acid on the application of heat. The acid corresponding to the lactone is not capable of existing as such; its salts, however, are known. PCl₅ converts the lactone into anthraquinone (B. 21, 2005). o-Cyanbenzhydrol, $C_6H_6(CHOH)C_6H_4[2]CN$, has been prepared from o-cyandiphenylchlormethane, C_6H_6CHCl , the reaction product from chlorine

and cyandiphenylmethane (B. 29, 1315). m- and p-Benzhydrylbenzoic Acid melt at 121° and at 164° (A. 220, 242). p-Tolylphthalide melts at 129°; for its homologues see A. 234, 237. Oxyphenylphthalide, C₆H₄ (CO) , melting at 180°, is obtained from phthalaldehydic acid (p. 236), phenol, and sulphuric acid (73 per

cent.) (B. 27, 2632). Benzhydrol-o₂-lactone Carboxylic Acid, C₈H₄ CH—C₆H₄CO₂H , melting at 202°,

is produced on heating benzhydroltricarboxylic acid mono-lactone, C_6H_4 . CO_2H_4 . CO_2H_4 .

the reaction-product of alkalies upon diphthalic acid (A. 242, 233). C. Benzophenone Carboxylic Acids are formed (I) in the oxidation of the alkyldiphenylmethanes, alkylbenzophenones, diphenylmethane carboxylic acids, and benzhydrol carboxylic acids; (2) from benzoyl chloride and benzoic anhydride with vinc malachite-green and rosaniline groups, as the leuce-derivatives of which they a quently designated; (3) by the condensation of benzhydrol or benzaldehyde and hydrochloride, or dimethyl aniline hydrochloride with P₂O₅ or ZnCl. When or with chloranil, or PbO₅ and hydrochloric acid, etc., their salts change to those color-bases to which malachite-green and rosaniline belong; they are derived fr phenyl carbinol.

m Amidotriphenyl Methane, (CaHb), CHC6H4[3]NH2, melting at 120°, is ol

from m nitrotriphenylmethane (B. 21, 189).

p-Amidotriphenyl Methane, melting at 84°, is formed (1) from p-aitrotri methane (B. 23, 1023), and (2) from benzhydrol, aniline hydrochloride, and zinc c

(A. 206, 155).

p-Dimethylamidotriphenyl Methane, $(C_8H_6)_2$ CH. $C_8H_4[4]N(CH_3)_3$, mel 132°, is formed from benzophenone chloride and dimethyl aniline, as well as from hydrol and dimethyl aniline with P_3O_5 (A. 206, 113). as well as from benzoph dimethyl aniline, and zinc chloride (A. 242, 341). p-Acetamidotriphenyl Memelts at 176° (B. 24, 728).

p. Diamido-triphenyl Methane, C₄H₆. CH(C₄H₄[4]NH₂)₂, melting at 1; C₄H₆ at 106°, the parent substance of malackite-green, is obtained (1) from chloride and aniline with zinc-dust; (2) from benzaldehyde with aniline hydrod on heating with zinc chloride to 120° (B. 15, 676), or by boiling benzaldehyd aniline and hydrochloric acid (B. 18, R. 334); (3) by reducing diamidotriphen

binol chloride with zinc-dust.

p₁-Tetramethyl-diamido-triphenyl Methane, C₆H₅. CH[-[4]N(CH₃)₂]₂, leucomalachite-green, is dimorphous, and crystalliz leaflets, melting at 93–94°, or in needles, which melt at 102°. The modification is obtained pure by crystallization from alcohol, the se from benzene. It is obtained by methylating p₂-diamido-triph methane, as well as by the action of benzaldehyde upon dimethyl an Technically, it is made by the condensation of benzaldehyde dimethyl aniline with hydrochloric or sulphuric acid (formerly chloride or oxalic acid). By oxidation it becomes p₂-tetramethyld do-triphenyl carbinol, the basis of malachite-green.

o. and m.Nitro.p₂.diamido-triphenyl Methane are produced in the condensal o. and m.nitrobenzaldehyde with aniline sulphate by means of zinc chloride. m.body melts at 136° (B. 13, 671; 16, 1305).

p-Nitro p₂-diamido-triphenyl Methane is obtained from p-nitrobenzaldehyd as the o- and m-compounds are prepared. See p-leucaniline (B. 25, 676).

Benzaldehyde and the nitrobenzaldehydes condense with o- and p-toluidine, j they do with aniline and dimethyl aniline (B. 18, 2094), whereas m-toluidin m-derivatives of aniline only react readily if the amido-group is methylated (1 1563).

Triamidotriphenyl Methanes result from the reduction of nitro- and nitroamidotriphenyl methanes and of the triamidotriple carbinols. The latter are the rosaniline bases if the three amido-goccur in the p-position with reference to the C(OH) group. Their duction products are also called leucanilines. These are white cipitates, and when oxidized yield the carbinols:

o,p₃. Triamidotriphenyl Methane, or o-Leucaniline, and m,p₂. Triamidotriphenyl Methane, or Pseudoleucaniline, and p₃. Triamidotriphenyl Methane, or Paraleucaniline,

which, upon oxidation, yield dyestuffs. That from the o-body is b in color, that from the m-body is violet, while that from the p-comp

is pararosaniline (p. 356). p-Triamidotriphenylmethane is also produced in the condensation of p-amidobenzaldehyde and aniline with zinc **chloride**; its tridiazochloride, CH(C₆H₄. N₂Cl)₃, when boiled with alco-

hol, forms triphenylmethane.

p₃-Triamido-diphenyl-m tolyl Methane, Leucaniline, (NH,[4]-C₆H₄)₂CH. C₆H₃[4](CH₂). NH₂[3], is the leuco-compound corresponding to the chief constituent of rosaniline obtained by the reduction of trinitro-diphenyl meta-tolyl methane, and is also made by digesting the fuchsine salts with ammonium sulphide, or zinc-dust and hydrochloric acid. By diazotizing and replacing the diazo-groups by hydrogen (best by dissolving in concentrated sulphuric acid, conducting nitrous acid into the same, and boiling with alcohol) leucaniline is changed into diphenyl-m-tolyl methane.

2. Carbinols are formed by oxidizing the triphenyl methane hydro-

carbons, their nitro- and amido-compounds.

Triphenyl Carbinol, (C₆H₅)₃C. OH, melting at 159°, boils without decomposition above 360°, and is produced by oxidizing triphenylmethane with chromic acid in glacial acetic acid (B. 14, 1944), on boiling triphenyl-brom-methane or triphenylchlormethane with water (B. 7, 1206), or with a soda solution, as well as from pararosaniline (B. 26, 2125), and from oxalic ester, or benzaldehyde, or benzophenone with sodium and brombenzene in ether (B. 28, 2514). The methyl ether melts at 82°, and the acetate at 99° (A. 227, 116).

Diphenyl-m-tolyl-carbinol, $(C_8H_5)_2$. C(OH). $C_6H_4[3]CH_8$, melting at 150°, is prepared from diphenyl-m-tolyl methane in the same manner as with triphenyl carbinol (A. 194, 283).

Triphenylchlormethane, Triphenyl Carbinol Chloride, (C6H5)3CCl, melting at 105-115°, results upon treating triphenyl carbinol with PCl₅, and by the action of aluminium chloride upon carbon tetrachloride in benzene solution. When heated above 250° it

breaks down into diphenylene phenyl methane, C_6H_5 . $CH < \frac{C_6H_4}{C_6H_4}$, and hydrochloric acid.

Triphenyl-brom-methane, (C₆H₅)₃CBr, melting at 152°, is produced when bromine acts in sunlight upon triphenylmethane dissolved in carbon disulphide (A. 227, 110). Above 2000 it breaks down like the chloride. Potassium cyanide transposes it into tri-

Above 200° it breaks down like the carrier phenylacetonitrile (p. 370).

Triphenyl-methylamine, Triphenylcarbinolamine, (C₆H₅)₃C. NII₂, melting at 103°, is produced on conducting dry ammonia gas into a benzene solution of triphenylcarbinol bromide or chloride (B. 17, 442, 741). Triphenylcarbinolphenylamine, (C₆H₆)₃C. NH. C₆H₆, melts at 144° (B. 17, 703, 746).

Diphenylbenzylsultam, C₆H₄ { [1]C(C₆H₆)₂ NH₂, melting at 210°, may be sinkenylmethylamine. It is formed, together with phenylbenzalsultime (p. 346), in the condensation of pseudosaccharin chloride with benzene and Al_Cl₆ (B. 29, 2296). m- and p-Nitrotriphenyl-carbinol, $(C_6H_6)_2C(OII)C_6H_4NO_2$, melt at 75° and at 136° (B. 21, 190; 23, 1623).

p₃-Trinitrotriphenyl Carbinol, (NO₂[4]C₆H₄)₃. C. OH, melting at 171°, is prepared from p₃-trinitrotriphenyl methane by the action of chromic acid in glacial acetic acid. It yields p-rosaniline upon reduction.

Amidotriphenyl Carbinols.—p₂-Diamidotriphenyl-carbinol and p₂-triamido-carbinols, of this class, deserve especial consideration. p₂-Tetramethyldiamidotriphenyl-carbinol is the basis of malachite-green and p₃-triamidotriphenyl-carbinol that of p-rosaniline. The free amidocarbinols are colorless. In contact with acids water is eliminated and color-salts result. These are also formed by the direct oxidation of the salts of the leuco-compounds, and pass into the latter upon reduction. Thus, p-leucaniline hydrochloride (1) yields, upon oxidation, p-rosaniline chloride, from which colorless p₃-triamidotriphenyl-carbinol is separated by bases; hydrochloric acid converts this compound again into p-rosaniline chloride:

$$\frac{\text{NH}_{2}[4]C_{6}H_{4}}{\text{NH}_{2}[4]C_{6}H_{4}}C \\ \\ \frac{\text{C}}{\text{H}} \\ \frac{\text{C$$

The formula of p-rosaniline chloride can be more conveniently written than shown in the diagram by assuming it to be derived rather from the diketo formula than from the superoxide formula of quinone-imide (p. 172), and the valence of the nitrogen still be considered as five:

$$(NH_{2}[4]C_{6}H_{4})_{2}C = C_{6}H_{4}[4] = NH_{2}Cl.$$

As the triamidotriphenyl-carbinols are considerably stronger bases than the corresponding triamidotriphenyl-methanes, and as two amidogroups behave differently than the third, the following constitutional formula has been suggested for p-triamidotriphenyl carbinol (B. 28, 207):

$$(NH_{2}[4]C_{6}H_{4})_{2}C.O(C_{6}H_{4}[4]NH_{3}).$$

m- and p-Amidotriphenyl Carbinol, (C₆H₅)₂C(OH)C₆H₄NH₂, melt at 155° and 116° (B. 21, 190; 23, 1625). The salts of these carbinols do not possess color-power.

p₂-Diamidotriphenyl Carbinol.—The chloride of this dye, soluble with a reddish-violet color, is produced on heating aniline hydrochloride, nitrobenzene, and benzotrichloride with iron filings (A. 217, 242).

 p_2 -Tetramethyl-diamido-triphenyl Carbinol, C_6H_5 . $C(OH)[C_6-H_4[4]N(CH_3)_2]_2$, melting at 132°, crystallizes from benzene in colorless forms. It is obtained from its salts (malachite-green) by precipitation with the alkalies and by oxidizing an alcoholic solution of p_2 -tetramethyl-diamido-triphenylmethane with chloranil (A. 206, 130).

The free base yields almost colorless solutions with acids in the cold; upon standing, more rapidly on heating, the solution acquires a green color and then contains the green salts—malachite-greens—of the anhydrobase of the carbinol (B. 12, 2348).

Malachite Green, Bitter Almond Oil Green, C₆H₅. C_{C₆H₄N(CH₃)₂Cl,}

the hydrochloride of the anhydro-base, is produced when zinc chloride acts upon a mixture of benzotrichloride and dimethylaniline, or upon a mixture of benzoyl chloride and dimethyl aniline (A. 206, 137).

Technically, leucomalachite green is first prepared and its hydrochloride then oxidized with lead peroxide. Upon heating to 200° with concentrated hydrochloric acid it breaks down into dimethyl aniline and p-benzoyldimethyl aniline (p. 347). The iodmethylate, $C_6H_6C(OCH_3)[C_6H_4N(CH_3)_3l]_2 + 2H_2O$, is obtained on heating p_2 -diamido-triphenyl-carbinol and p_2 -tetramethyldiamido-triphenyl-carbinol with methyl iodide and methyl

Malachite green, characterized by its strong coloring power, usually appears in trade in the form of its sinc chloride double salt, (C23H25N2Cl)3. 2ZnCl2 + 2H2O, or its oxal-

ate, (C₂₃H₂₅N₂)₂₃C₂O₄H₂.

History.—Malachite green, or bitter almond oil green, was obtained in 1877 by O. Fischer in the oxidation of p₂-tetramethyldiamido-triphenyl methane. He obtained to the control of the contr the latter compound by condensing benzaldehyde with dimethylaniline. Doebner (1878) showed how malachite green could be prepared from benzotrichloride and dimethyl

Brilliant Green, Solid Green, New Victoria Green, is the tetra-ethyl derivative, corresponding to malachite green, which is made from diethylaniline and benzaldehyde (B.

14, 2521). The color is more yellow-tinted than that of malachite green.

Acid Green is a dye obtained from benzaldehyde and benzyl-ethyl aniline by condensation, oxidation, and sulphonation. The sulpho-groups are in the benzyl residue (B. 22, 588).

Nitromalachite Greens have been prepared with o-, m-, and p-nitrobenzaldehydes

and dimethyl aniline as the starting-out substances (B. 15, 682).

Triamidotriphenyl Carbinols.—p2-Triamidotriphenyl carbinol, p8triamidodiphenyl-m-tolyl carbinol, and their methyl, ethyl, benzyl, and phenyl derivatives, are of the highest importance for the coal-tar color industry. Their salts with one equivalent of acid, hydrochloric or acetic, constitute the group of rosaniline dyes in the more restricted sense. Like malachite green, the rosaniline dye-substances are free from carbinol oxygen, as the salt formation is accompanied by an intramolecular anhydride formation. The carbinols separated from these salts by alkalies are colorless, but turn red, however, on exposure to the air.

Fuchsine is the dyestuff produced in the oxidation of a mixture of aniline, o-toluidine, and p-toluidine. It is the so-called red oil (p. 76). Rosaniline is the chief ingredient of fuchsine. It is the hydrochloride or acetate of anhydro-p₃-triamidodiphenyl-m-tolyl carbinol, C₂₀H₁₉N₃. HCl + 4H₂O or C₂₀H₁₀N₃. C₂H₄O₃. The monacid salts combine with two additional equivalents of acid, forming yellowish-brown colored salts, which water decomposes into the stable, monacid salts with intense colors. These are applied as dyes. They are mostly readily soluble in water and alcohol, and crystallize in metallic, greenish crystals. Their solutions are carmine-red in color, and stain animal tissue directly violet-red, while vegetable fiber (cotton) must first be mordanted (tannin). Fuchsine combines with sulphurous acid, forming the readily soluble, colorless fuchsine-sulphurous acid.

Aldehydes impart a red color to this solution, which serves as a reagent for them.

Oxidants used with red oil (p. 76) are stannic chloride (Verguin, 1859), mercurous and mercuric nitrates, arsenic acid at 180-200° (Medloc, Nicholson, Girard and de Laire, 1860); nitrobenzene with a little ferrous chloride or ammonium vanadate at 180-1900, when the half of the red oil is applied as hydrochloride (Coupier, 1869; compare B. 6, 25, 423, 1072).

In the arsenic acid method the fuchsine is obtained in the form of arsenites, which are then converted into the chlorhydrate or acetate, and obtained free from arsenious acid by

recrystallization.

The nitrobensene method yields immediately a fuchsine which is not poisonous. The nitrobenzene only acts as an oxidant, without entering into the fuchsine formation at all.

Fuchsine is not formed either from aniline or from p-toluidine, or from o-toluidine alone. Even a mixture of aniline with o-toluidine is not oxidized to fuchsine. However, not only a mixture of aniline with o- and p-toluidine yields fuchsine, but in the oxidation of a mixture of aniline and p-toluidine a dye, with the properties of fuchsine, called pararosaniline, is produced. This is also present in small amount in the fuchsise made from aniline and o- and p-toluidines; whereas the principal constituent of ordinary fuchsine consists of the next higher homologue of pararosaniline, namely, rosaniline (B. 13, 2204).

By-products in the Formation of Fuchsine.—The fuchsine melt contains, in addition to 34 per cent. of fuchsine, other violet and brown dyes: manuaniline, violaniline, substances belonging probably to the indulines, and other less thoroughly investigated substances, as well as slight amounts of a yellow acridine dye, known as phosphin or

chrysanilin (see this).

History of the Recognition of the Constitution of Rosaniline and Pararosaniline.— A. W. Hofmann was the first person to engage in a scientific study of fuchsine. He began his investigations in the sixties, and was led, as a consequence, to present a formula for fuchsine and its fundamental dye-base. He became acquainted with numerous derivatives of fuchsine, especially the methyl and ethyl violet fuchsines. He assumed that the nitrogen atoms held together the radicals in the fuchsine molecule. However, Kekulé (1867) argued for the possibility that the methyl groups of the toludine molecules, necessary for the production of fuchsine, afforded the connection. K. Zulkowsky (1869) assumed the presence of three amido-groups in fuchsine, and considered it a derivative of a hydrocarbon with the formula C₁₈H₁₄. Gradually, however, the conviction grew that fuchsine sprang from a higher aromatic hydrocarbon. This idea had its basis or origin in the experiments of Wanklyn, Caro, Graebe, Dale, Schorlemmer, and thurs, which in the main established the relationship of fuchsine to receive a city. The others, which, in the main, established the relationship of fuchsine to rosolic acid. The "keystone to that extended series of experimental and speculative investigations" was the conversion (1878) of pararosaniline, prepared by the oxidation of aniline and p-toluidine, into triphenylmethane. This was the work of Emil and Otto Fischer. The hydrocarbon prepared by them from rosaniline, the chief constituent of fuchsine, proved to be diphenyl-m-tolylmethane.

Triphenylmethane (4) is formed in the decomposition of the tridiazosulphate of paraleucaniline with alcohol. In the diagram the formula of the tridiazochloride (3) of paraleucaniline (2) is used for the sake of simplicity. Concentrated nitric acid convers triphenylmethane into p₃-trinitrotriphenylmethane (5), which, upon reduction, yields p₃-triamidotriphenylmethane, or paraleucaniline (2). The latter, by oxidation is converted into ps trinitrotriphenyl carbinol (6). On oxidizing paraleucaniline with arsenic acid, or by reducing p₃-trinitrotriphenyl carbinol with acetic acid and zinc-dust, pararosaniline (1) results. The following diagram illustrates this series of reactions, which

were carried out, beginning with rosaniline itself (A. 194, 242):

$$\begin{vmatrix} (1) & C & C_6H_4[4] N H_2 & 2H & C_6H_4[4] N H_2 \cdot H C I \\ C_6H_4[4] N H_2 & 2H & C_6H_4[4] N H_2 \cdot H C I \\ C_6H_4[4] N H_2 & 2H & C_6H_4[4] N H_2 \cdot H C I \\ C_6H_4[4] N H_2 & C_6H_4[4] N H_2 \cdot H C I \\ C_6H_5 \cdot H I \\ C_6H_5 \cdot$$

Pararosaniline is produced by oxidizing a mixture of aniline and p-toluidine according to the arsenic acid or nitrobenzene method (p. 355). The reaction may be imagined to proceed in that a molecule of p-toluidine is oxidized to p-amidobenzaldehyde, the latter then condenses with two molecules of aniline to paraleucaniline or ps-triamidotriphenylmethane (p. 355), from which, finally, pararosaniline results by oxidation.

When working with small quantities the most convenient way of oxidizing aniline and p-toluidine to pararosaniline consists in using mercuric chloride (B. 24, 3552). An interesting formation of pararosaniline is that of heating aniline with carbon tetrachloride to 230°, when the latter furnishes the linking carbon atom. The hydroiodide of para-

rosaniline results by using iodoform, CHI₂.

Pararosaniline is further formed by the reduction of p₃-trinitrotriphenyl carbinol (see above); by heating p₃-nitrodiamido-triphenyl methane with ferrous chloride (B. 15, 678); triamidotriphenyl carbinol is also formed by moderated reduction of p-nitrodiamido-triphenylmethane, inasmuch as the diamido-diphenylmethane-phenylhydroxylamine, (C₆H₄NH₂)₂CH. C₆H₄. NHOH, formed at first, rearranges itself (B. 29, R. 32); further, by heating p-diamido-diphenylmethane with aniline and some oxidizing agent (B. 25, 302); by heating p-nitro-benzal chloride with aniline (B. 18, 997), and by heating aurine to 120° with aqueous ammonia (B. 10, 1016, 1123).

Nitrous acid converts it into aurine. Triphenyl carbinol results when pararosaniline diazochloride is decomposed with finely divided copper (B. 26, 2225). At 180-200° pararosaniline is converted by concentrated hydriodic acid into aniline and p-toluidine. Evidence favoring the p-position of the two amido-groups is found in the conversion of p-rosaniline by boiling hydrochloric acid into p₂-diamido-benzophenone, which is also obtained from p diamido-triphenylmethane, the condensation product of benzaldehyde with aniline. Paraleucaniline, the reduction product from pararosaniline, is also formed by the reduction of p₂-nitrodiamido-triphenyl methane. The p-position of the three groups in the latter compound follows from the fact that it is produced by the same condensation reaction from p-nitrobenzaldehyde and aniline by which p-diamido-triphenylmethane is made from benzaldehyde and aniline.

In addition to the two constitution formulas (I and II) already given for the hydrochloride of pararosaniline, a third (III) may be offered; this would represent it as partiamido triphenyl carbinol chloride:

I.
$$NH_{2} \cdot C_{6}H_{4} > C < \frac{C_{6}H_{4}NH}{C_{6}H_{4}} + HCl$$
 (E. and O. Fischer).

II.
$${NH_2 \cdot C_6H_4 \atop NH_2 \cdot C_6H_4} > C = C_6H_4 = NH \cdot HCl$$
 (Nietzki).

Also compare B. 29, 2677, R. 346, in regard to the constitution of the rosaniline bases.

The rosaniline salts give a deeper blue shade than the salts of para-rosaniline (B.

15, 680).

Homologous Rosanilines have been prepared by the oxidation of a mixture of aniline and unsym. metaxylidine (B. 15, 1453), by condensation of p-nitrobenzaldehyde with o-toluidine, reduction and oxidation of the resulting condensation product (B. 15, 679), and by the condensation of p-nitrodimethylamidobenzhydrol with m-toluidine, etc. (B. 24, 553).

Rosaniline Sulphonic Acid, Acid Fuchsine, Fuchsine S, is produced in the action of sulphuric acid at 120° upon rosaniline.

Alkylic Rosanilines.—The introduction of methyl residues into the amido-groups of rosaniline produces violet dyes-methyl violet. violet color assumes a deeper blue tint with the increase of methyl groups. These dyes are made by methylating pararosaniline and by oxidizing dimethyl aniline. The methyl violets are reduced to leuco-compounds when they are heated with ammonium sulphide to 120°. Boiling hydrochloric acid resolves them into dimethyl aniline and methylated pdiamido-benzophenones (B. 19, 108).

Hexamethyl Pararosaniline, Crystal Violet, [(CH₃)₂N. C₆H₄]₂. $C = C_4H_4 = N(CH_4)_2Cl$, is distinguished from the lower methyl derivatives by great power of crystallization. It forms one of the principal constituents of methyl violet, and is produced (1) by the condensation of p₂-tetramethyldiamido-benzophenone and dimethyl aniline with dehydrating agents:

(2) By heating dimethylaniline with COCl₂ and AlCl₂ or ZnCl₂ (B. 18, 767; R. 7). Formic acid, formic ester, chlorcarbonic ester, perchlormethyl mercaptan, CSCl₂, etc., act the same as phosgene (B. 19, 109); (3) by oxidation of p₂-tetramethyldiamido-diphenyl methane with dimethyl aniline; (4) by heating its methyl chloride or iodide to 110-120°; (5) by oxidizing its leuco-base.

p3. Hexamethyl Triamidotriphenyl Carbinol, Crystal Violet Base, C(OH)[CeH4-

[4] N(CH₃)₂]₃, melts at 195°.

p₃: Hexamethyl Triamidotriphenyl Methane, Leuco-crystal Violet, CH[C₈H₄[4]-N(CH₃)₂]₃, melting at 173°, results by the reduction of crystal violet, by the condensation of ortho-formic ester and dimethyl aniline with ZnCl₂, and by the condensation of p₃-tetramethyldiamido-benzhydrol with dimethyl aniline.

Methyl Violet is a mixture of hexamethylpararosaniline with lower methylated derivatives (B. 19, 107). It is produced in oxidizing dimethyl aniline, alone or when mixed with monomethyl aniline, with iodine or chloranil, copper sulphate or chloride. When copper chloride is used it is advisable to add acetic acid or phenol.

Pentamethyl Violet, $C_{19}H_{12}N_3(CH_3)_5HCl$, is formed by oxidizing p₃-pentamethyltriamidotriphenylmethane, $[(CH_3)_3NC_8H_4]_2CH$. $C_6H_4[4]NH$. CH_3 , melting at 116°. The latter can be isolated from the reduction-product of commercial methyl violet, a mixture of penta- and hexamethyl violet, by means of the acetyl derivative. This, when oxidized with acetylpentamethyl rosaniline, yields a green dyestuff (B. 16, 2906).

Tetramethyl Violet is formed by oxidizing p₃-amidotetramethyldiamidotriphenylmethane, melting at 152°. The latter is a tetramethylparaleucaniline,
Nl1₂[4] C₆l1₄Cl1[C₆H₄][4]N(CH₃)₃], produced in the reduction of p-nitromalachitegreen. Its acetyl derivative, like that of pentamethyl-leucaniline, yields a green dye upon
oxidation.

Methyl Green, Methyl Chloride of Hexamethyl-pararosaniline Chloride,

 $Cl(CH_3)_3N[4]C_6H_4C < C_6H_4[4]N(CH_3)_2C_1$, is produced when methyl chloride acts upon

an alcoholic solution of methyl violet heated to 40°, sodium hydrate being gradually added.

Alkylic Rosanilines.

When rosaniline is heated with methyl iodide, methyl chloride, ethyl iodide, or chloride, and methyl or ethyl alcohol, three amide hydrogen atoms are replaced by methyl or ethyl radicals. The methyl base yields reddish-violet-colored salts (*Hofmann's Violet, Dahlia*); these dissolve with difficulty in water, but dissolve easily in alcohol.

The violet dyes, by the addition of more methyl or ethyl groups, yield tetra-alkylic rosaniline iodides, which are capable of adding another molecule of methyl or ethyl iodide and forming iodine greens—e. g., iodmethylate of tetramethyl rosaniline iodide, C₂₀H₁₆(CH₃)₄N₃I.-CH₃I + H₂O, which has been displaced in the dye industry by methyl green (see B. 28, 1008).

Aldehyde Green (Usèbe, J. pr. Ch. 92, 337), another green rosaniline dye, has been prepared by heating rosaniline with aldehyde and sulphuric acid, and by further action of sodium hyposulphite. The most recent opinion is that in this reaction an aniline group has been changed to quinaldine, while the other two groups have occasioned the formation of aldol aniline residues, which latter then add sulphur, just as is done by aldol aniline itself (p. 79) (compare B. 24, 1700; 29, 60).

Phenylated Pararosanilines. - Just as methyl violet is prepared from dimethyl ani-

line by means of COCl₂, etc., so

Diphenylamine Blue can be obtained by heating diphenylamine with carbon hexachloride, C_3Cl_6 , or oxalic acid, to 120°. It is identical with *triphenylpararosaniline*, C-(OH)(C_6H_4 . NH. C_6H_6)₃ (B. 23, 1964), obtained by the action of aniline upon pararosaniline. At present it is only the sodium salts of its mono- and disulpho-acids which are applied as Alkali Blue and Water Blue in dyeing.

Perchlorformic ester, CClO₂CCl₂, in a similar manner converts diphenyl methylamine,

(CaHa)2N. CH2, into trimethyl-triphenyl-pararosaniline,

 $C(OH)(C_8H_4. N C_8H_5)_8$ (B. 19, 278). Phosgene converts triphenylamine into the hydrochloride of hexaphenyl-pararosaniline, $C(OH)[C_6H_4. N(C_6H_5)_2]_3$ (B. 19, 758). Tricarbazole Carbinol, $C(OH)(C_{12}H_1NH)_3$ (B. 20, 1904), is produced by heating together carbazole and oxalic acid. It is analogous to the triphenylamine derivative.

Phenylated Rosanilines are obtained by heating rosaniline hydrochloride with aniine or toluidines, or the free base with aniline and some benzoic acid. The triphenylrosaniline hydrochloride, C₂₀H_{ie}(C₆H₅)₃N₈. HCl, appeared in commerce as aniline blue, a bluish-brown crystalline powder with copper luster, soluble in alcohol but not in water. To dissolve it in the latter, sulpho salts are prepared, which exhibit different shades of blue (soluble blue) corresponding to the number of sulpho-groups in them. At present diphenylamine blue and other dyes have taken its place. Diphenylamine results on distilling triphenyl-rosaniline.

By converting rosaniline, by means of the tridiazo-compound into the trihydrazine derivative, there results Roshydrazine, C(OH)(C₂H₅. NH. NH₂)₃; this, by condensation with aldehydes and ketones, yields red and blue dyestuffs (B. 20, 1557).

3. Phenol Derivatives of the Triphenylmethanes.—The phenol derivatives of the triphenylmethanes are produced (1) from the corresponding amido-compounds through the diazo-derivatives; (2) by condensations similar to those of the amido-compounds if phenols be substituted for the anilines; (3) by the reduction of the phenol carbinols, into which they are changed by oxidation.

Monoxytriphenyl Methanes.- In this class may be included o-Diphenyl Cresol, o-Oxytriphenyl Methane, (C₆H₆)₂CH. C₆H₄[2]OH, melting at 118°. It is obtained from o-amidotriphenyl methane (A. 241, 367). Oxydiamidotriphenyl Methanes (B. 14, 2522; 16, 1307) are produced by the condensation of salicylaldehyde and anisaldehyde with aniline sulphate or dimethyl aniline and zinc chloride.

The di- and tri-oxytriphenyl methanes yield, on oxidation, diand triphenol carbinols, which, as a rule, possess the character of dyesubstances. Carbinols in which two benzene nuclei are hydroxylated, and which correspond to the malachite-green compounds, are termed benzeines; whereas the derivatives with three hydroxylated benzene nuclei are called aurines or rosolic acids, while corresponding trioxytriphenylmethanes are designated as leucaurines or leuco-rosolic acids.

.-Dioxy-triphenyl Methane, Leucobenseine, leucobenzaurine, Calla. CII(Calla-[4]OH), is obtained (1) from p₂-diamido-triphenyl methane (p. 352) (A. 206, 153) (2) by reducing bensaurine (A. 217, 230), as well as (3) by the condensation of beamlehyde and phenol with sulphuric acid (B. 22, 1944). It melts at 161°.

Dioxydimethyl Triphenyl Methane, C₆H₆CH_{[C₆}H₂(OH)CH₂], melts at 170° (A. 257, 70). Phenyldithymol Methane melts at 165°.

See B. 24, R. 562, for the condensation of m-nitrobenzaldehyde with phenols.
p. Trioxy-triphenyl Methane, Leucaurine, [Triphenylol Methane], CH(C,H,[4]-OH), is obtained in the reduction of aurine, its carbinol anhydride, by means of zine-date. and sodium hydrate or acetic acid. It crystallizes in coloriess needles, which become colored on exposure to the air (A. 166, 286; 194, 136; 202, 198). The triacctate mells at 138° (B. 11, 1117).

Leuco-rosolic Acid, (HO[4]C₈H₄)₂. CH. C₈H₄[4]OH[3]CH₂, results from the reduction of rosolic acid. Its triacetate melts at 148° (A. 179, 198).

4. Phenol Derivatives of Triphenyl Carbinol.—A. Benselnes (see above) are produced by the condensation of benzotrichloride with mono- and polyhydric phenols, in which the para-position with reference to a hydroxyl group is not substituted—e.f., o- and m-cresol, resorcinol, and pyrocatechin (but not p-cresol, hydroquinone, etc.) (R. 23, R. 340). They are also formed when their leuco-compounds, the corresponding oxytriphenyl methanes, are oxidized.

The benzeines are generally red-colored compounds with metallic luster. They dissolve on boiling with sodium bisulphite; acids reprecipitate them. Alkalies dissolve them with the formation of red or violet-colored salts. The carbon dioxide of the six

decomposes the latter.

p₁-Dioxy-triphenyl Carbinol, *Phenol Benzeine*, *Benzeurine*, C₆H₆. C

CH OV

or C_6H_5 . $C < C_6H_4$. OH is produced in the condensation of benzotrichloride and phenol (similar to the formation of malachite-green) (A. 217, 223), and by the oxidation of phenol dioxytriphenylmethane, into which it passes upon reduction. It is a brick-red, crystalline powder. It breaks down, when fused with alkalies, into benzene and dioxybensophenone, and this latter decomposes further into paraoxybenzoic acid and phenol. Its diacetate melts at 119°.

p, Dioxy m, dimethyl Triphenylmethane, o-Cresol Benzeine, C,H, C(OH). [C₆H₃[3]CH₃[4]OH]₂, melts at 220-225° (A. 257, 69).

 $C_6H_5C[C_6H_3(OH)_2]_2$

Resorcinol Benzeine, C₃₈H₃₀O₉ = , is formed when water

C₆H₅C[C₆H₅(OH)₉]₉ acts upon the reaction product of resorcinol and benzotrichloride (A. 217, 234), and when ZnCl, acts upon benzoic acid and resorcin (J. pr. Ch. [2], 48, 387). See B. 26, 2064,

for dinitro esorcinol benzeine.

Rosamines.—These are derivatives of diamido-benzelnes. They are formed when mono-alkylic and dialkylic o-amidophenols act upon benzotrichloride. While the benzeines, from phenols, are very seeble dyes, whose alkali salts are even decomposed by carbon dioxide, the hydrochlorides of the rosamines are red and violet dyes, having great similarity to the rhodamines (p. 366), but possessing a blue tint and redder floor. escence (B. 22, 3001). They also result on heating resorcinol benzeine with dimethyl and diethyl aniline.

Rosamine Chloride, C_6H_5C $C_6H_5\begin{bmatrix}4\\2\\2\\0\\C_6H_8\end{bmatrix}$, may be obtained from beam-

trichloride and dimethyl aniline. It forms reddish-black needles with a steel-black reflex.

B. Aurines and Rosolic Acids.—These compounds correspond perfectly to the rosanilines. The free ps-trioxy-triphenyl carbinols are not known. When freed from their salts they sustain an intramolecular anhydride formation.

These carbinol anhydrides are yellow in color; their alkali salts dissolve in water,

with a red color. They are incompletely fixed by the fiber of the material, and are only applied in the form of lakes in the paper industry.

Aurine, Para-rosolic Acid, Yellow Corallin, $HO[4]C_6H_4 > C < C_6H_4[4] > O$, is produced (1) on boiling the diazohydrochloride of pararosaniline with water (A. 194, 301); (2) by the condensation of p-dioxybenzophenone chloride with phenol (B. 11, 1350); (3) by the condensation of phenol with formic acid on heating with zinc chloride (J. pr. Ch. [2], 23, 549); and (4) by heating phenol (1 part) with oxalic (½ part) acids to 130–150° (A. 202, 185). For the by-products arising when surine is prepared by method 4, and for its separation from the same, see A. 194, 123; 196, 77; B. 28, R. 743.

Aurine dissolves in glacial acetic acid and alcohol, crystallizes in dark red needles or prisms with metallic luster, and decomposes when heated above 220°. It dissolves in alkalies with a fuchsine-red color. With the primary alkaline sulphites it readily yields colorless, crystalline derivatives, decomposable by acids and alkalies. Aurine forms crystalline compounds with hydrochloric acid. Water decomposes them. Digested with zinc-dust and hydrochloric acid or acetic acid, aurine is reduced to leucaurine or p₃-trioxy-triphenylmethane. Heated to 250° with water, it breaks up into p₃-dioxy benzophenone

and phenol.

Aurine is changed to pararosaniline when it is heated with aqueous ammonia to 150°. An intermediate product (having I or 2 amide groups) is the so-called *Peonine* (red corallin). With aniline we obtain triphenyl-rosaniline, and the intermediate product is *Azuline*. Consult B. 29, R. 510, for isomeric acetyl-aurines.

Rosolic Acid, $C_{20}H_{10}O_{3}$, is the inner anhydride of p_3 -trioxydiphenyl-m-tolylcarbinol. Rosolic acid, like aurine, is obtained by boiling the diazochloride of rosaniline with water (A. 179, 192) and by oxidizing a mixture of phenol and cresol, $C_6H_4(CH_3)OH$, with arsenic acid and sulphuric acid, whereby the linking methane carbon is furnished by the methyl group. When rosolic acid is digested with alcohol and zinc-dust, it is reduced to leucorosolic acid, from which it is obtained by oxidation (B. 26, 254).

Trioxy-aurine, $C_{19}H_{14}O_6$, results from the interaction of ZnCl₂, pyrocatechine, and formic acid (B. 26, 255). Resaurine, $C_{19}H_{14}O_6$, is similarly prepared with resorcinol (J. pr. Ch. [2], 23, 547). Orcin-aurine, $C_{22}H_{18}O_5$ (J. pr. Ch. [2], 25, 277; B. 13,

546).

Eupittonic Acid, Eupitton, Hexamethoxy-aurine, C₁₉H₈(OCH₃)₆O₃, is produced by oxidizing a mixture of the dimethyl ester of pyrogallic acid and methyl pyrogallic acid. It is, therefore, an aurine in which six methoxyl groups are present. It forms orange-yellow crystals, melting with decomposition at 200°. It dissolves with a deep blue color in alkalies, yielding salts which are precipitated by excess of alkali (B. 12, 2216). Reichenbach (1835) observed the formation of a blue-colored barium salt when fractions of beechwood-tar were allowed to stand with baryta-water, and named it pittical (from πίττα, tar, and κάλλος, beautiful). When heated with ammonia, eupittonic acid, just like aurine, affords an hexamethoxyl-rosaniline.

5 and 6. Alcohols and Aldehydes of Triphenylmethane.—Few of them are known: Phenolphthalol, (HOC₂H₄)₂CIIC₆H₄[2]CII₂OH, melting at 190°, was pre-

pared by the action of sodium amalgam upon phenolphthalein (A. 202, 87).

p-Diphenylmethyl-benzaldehyde, (C₆H₅)₂CH[4]C₆H₄. CHO, boiling at 190–195° (46 mm.), results from the condensation of terephthalaldehyde and benzene with con-

centrated sulphuric acid (B. 19, 2029).

7. Carboxyl Derivatives of Triphenylmethane. — Triphenylmethane Carboxylic Acids are produced (I) by reduction of triphenyl carbinol carboxylic acids, and (2) from their nitriles. The latter are prepared by the action of aluminium chloride

spon the cyanbenzal chlorides (p. 238) and benzene.

Triphenylmethane-o-carboxylic Acid, Benzene Phthalin (see phthaleins, p. 363), (C₆H₅)₂CH. C₆H₄[2]CO₂H, melting at 162°, is isomeric with triphenyl acetic acid (p. 369), and is produced by the reduction of diphenylphthalide (2), the lactone of triphenylicarbinol-o-carboxylic acid (A. 202, 52), and from its nitrile. Chromic acid oxidizes it to diphenylphthalide, while it breaks down into carbon dioxide and triphenylmethane then it is heated with barium hydroxide. Sulphuric acid rearranges it to phenylanthranol (3):

$$\begin{array}{c} C_{\mathfrak{g}}H_{\mathfrak{s}} \\ C_{\mathfrak{g}}H_{\mathfrak{s}} > C < C_{\mathfrak{g}}H_{\mathfrak{s}}[2]CO \\ C_{\mathfrak{g}}H_{\mathfrak{s}} > C < C_{\mathfrak{g}}H_{\mathfrak{s}}[2]CO_{\mathfrak{g}}H \\ C_{\mathfrak{g}}H_{\mathfrak{s}} > C < C_{\mathfrak{g}}H_{\mathfrak{s}}[2]CO_{\mathfrak{g}}H \\ C_{\mathfrak{g}}H_{\mathfrak{s}} > C < C_{\mathfrak{g}}H_{\mathfrak{s}}[2]CO_{\mathfrak{g}}H \\ OH \end{array}$$

o-Cyantriphenylmethane, (CaH₅)₃CH. CaH₄[2]CN, melts at 89° and boils at 270-

285° (70-85 mm.). Preparation, see above (B. 24, 2572).
p. Tetramethyldiamidotriphenylmethane-o-carboxylic Acid, [(CH₃)₂N[4]C₁ II₄], CII. C₆II₄[2]CO₂H, from tetramethyldiamidodiphenylphthalide (p. 363) (A. 206, 101), melts at 200°.

Triphenylmethane-p-carboxylic Acid melts at 161°, and its nitrile at 91° (B. 26, 3079). Methyltriphenylmethane Carboxylic Acids—see B. 16, 2364; 19,

3064; A. 234, 242.

Oxytriphenylmethane Carboxylic Acids are formed in the reduction of the oxytiphenylcarbinol carboxylic acids. p-Oxytriphenylmethane-o carboxylic Acid,

HO[4]C₄H₄>CH . C₆H₄[2]CO₂H, melting at 210° (B. 13, 1616), and p.Dioxytriphenylmethane-o-Carboxylic Acid, *Phthalin*, [HO[4]C₆H₄]₁CH. C₆H₄[2]CO₄H, melting at 225° (A. 202, 36, 153), were obtained from the corresponding oxyliphenyl-carbinol-o-carboxylic acids (p. 363). Concentrated sulphuric acid converts them into the corresponding oxyphenylanthranols.

Hydrofluoranic Acid, $C_0H_4\left\{\begin{bmatrix}1\\C_0H_4\end{bmatrix}^2\right\}O$, melting at 226-228°, results on the reduction of functions

from the reduction of fluorane and tribromfluorane (p. 365). When the acid is distilled over lime xanthone (see this) and benzene result, while diphenylenephenylmethane (B. 25, 3586) is produced in its distillation over baryta or soda-lime.

Fluorescine, p. Dioxyhydrofluorane Carboxylic Acid, is the reduction product

of fluorescein (p. 365).

8. Carboxyl Derivatives of Triphenylcarbinol, Phthalides. The o-carboxyl derivatives of this class are especially noteworthy. They cannot exist free; they lose water and form lactones, which can be regarded as diphenylated phthalides (pp. 234, 349).

Diphenylphthalide, Triphenylcarbinol-o-carboxylic Acid Lactone, C_6H_4 $\left\{ \begin{bmatrix} x \end{bmatrix}C - (C_6H_5)_{1} \\ \vdots \end{bmatrix}$, melting at 115°, is formed (1) by the oxidation of ([2]COÒ

triphenylmethane-o-carboxylic acid, (2) in slight amount by the action of mercury diphenyl upon phthalylchloride, (3) from phthalylchloride and benzene with aluminium chloride. The third method of formation serves for the preparation of diphenylphthalide, formerly considered to be o-phthalophenone (p. 351), until it was discovered to contain a lactore, the basis of the phthaleins.

In the third method of producing diphenylphthalide the phthalyl chloride may be replaced by phthalic anhydride. In this case o-benzoylbenzoic acid will be the first product, which is the first product. uct, which by the further action of benzene and aluminium chloride changes to diphensiformation of disk acetyl derivative of o-benzoylbenzoic acid is better adapted for the

formation of diphenylphthalide than the free acid (p. 350) (B. 14, 1865).

Diphenylphthalide, when boiled with alkalies, forms salts of triphenylcarbinol-o-carboxylic acid from the salts of triphenylcarbinol-o-carboxylic acid from the salts of triphenylcarbinol-o-carboxylic acid from the salts are salts of triphenylcarbinol-o-carboxylic acid from the salts are salts as a salts of triphenylcarbinol-o-carboxylic acid from the salts are salts as a salts of triphenylcarbinol-o-carboxylic acid from the salts are salts as a salts of triphenylcarbinol-o-carboxylic acid from the salts are salts as a salts of triphenylcarbinol-o-carboxylic acid from the salts are salts as a salts a boxylic acid, from the solution of which acids re-precipitate diphenylphthalide. Zinc-dust in alkaling others solution of which acids re-precipitate diphenylphthalide. dust in alkaline solution of which acids re-precipitate dipnenyiphumano-o-carboxylic acid to triphenylcarbinol-o-carboxylic acid to triphenylmethaneThe anilide, C_6H_4 $\left\{ \begin{bmatrix} I \end{bmatrix}C = (C_6H_5)_2 \\ [2]CO.NH.C_6H_5 \\ \end{bmatrix}$, melting at 189°, and the hydrazide, C_6H_4 $\left\{ \begin{bmatrix} I \end{bmatrix}C = (C_6H_5)_2 \\ [2]CO.NH.C_6H_5 \\ \end{bmatrix}$, melting at 230°, are produced on boiling diphenylphthalide and aniline hydrochloride (B. 27, 2793) and with phenylhydrazine (B. 26, 1273). The nitration of diphenylphthalide produces two dinitrodiphenylphthalides, from which two diamidodiphenylphthalides have been obtained (A. 202, 66). p₃-Tetramethyldiamidodiphenylphthalide, C_6H_4 $\left\{ \begin{bmatrix} I \end{bmatrix}C = \begin{bmatrix} C_6H_4[4]N(CH_3)_2 \end{bmatrix}_2 \right\}$, melting at 190°, is obtained in the condensation of phthalic anhydride and dimethylaniline with ZnCl₂. If phthalic anhydride be substituted for phthalyl chloride in this

aniline with ZnCl₂. If phthalic anhydride be substituted for phthalyl chloride in this reaction there is an isomeric body, phthalyl-green, produced. This is probably an anthracene derivative (A. 206, 93).

Triphenylcarbinol-m-carboxylic Acid, melting at 161°, and Triphenylcarbinolp-carboxylic Acid, melting at 200°, are formed when diphenyl-m-tolylmethane and diphenyl-o-tolylmethane are oxidized with chromic acid in glacial acetic acid solution. The latter also appears in the oxidation of p-diphenylmethyl-benzaldehyde (p. 361),

and of triphenylmethane-p-carboxylic acid (p. 362) (B. 16, 2369; 26, 3081).

Phenyl-p-tolylphthalide is made from acetyl-o-benzoylbenzoic acid, toluene, benzoyl-o-benzoic acid chloride and toluene, toluic o benzoic acid chloride and benzene with aluminium chloride (B. 14, 1867; 29, R. 995). Isomeric methylated diphenylphthalides are produced in the oxidation of diphenyl-m- and p-xylylmethanes (p. 351). Ditolylphthalide melts at 116°. See B. 28, 513, for diphenylyl-o-phthalide,

 $C_{\mathbf{e}}H_{\mathbf{4}}\begin{cases} [1]CO.O \\ /\\ [2]C = (C_{\mathbf{e}}H_{\mathbf{4}}.C_{\mathbf{e}}H_{\mathbf{5}})_{\mathbf{5}}. \end{cases}$

Carboxyl Derivatives of the Oxytriphenyl Carbinols.

The Phthaleins, the derivatives of phthalide containing two phenol residues, are particularly important, and are dyes which are of great technical value. A. v. Baeyer discovered them in 1871. The transition from them to diphenylphthalide is found in-

Benzene Phenolphthalide, C_6H_4 $\left\{\begin{bmatrix}1\\2\end{bmatrix}CC_6H_5$ is prepared from 0-hencoult , melting at 155°.

It is prepared from o-benzoylbenzoic acid, phenol, and stannic chloride (B. 13, 1608). Benzene Resorcinolphthalide melts at 175°, and Benzene Pyrogallolphthalide melts at 189° (B. 14, 1859).

The Phthaleins result from the condensation of phthalic anhydride (1 mol.) with phenols (2 mols.) on heating with sulphuric acid, or, better, with ZnCl₂ to 120° (or with oxalic acid at 115°).

The phthaleins derived from di- and polyhydric phenols are all anhydrides, formed by the elimination of water from two phenol hydroxyls (A. 212, 347), in union with different benzene nuclei. In the condensation of phthalic anhydride and phenol p2-dioxydiphenylphthalide, or phenolphthalein, is not the only product; fluorane, the anhydride of o₂-dioxydiphenylphthalide is also formed. It is the simplest representative of the phthalein anhydrides, which contain a ring similar to the xanthone ring.

The free phthaleins are generally colorless, crystalline bodies. They dissolve in the alkalies with intense colorations, and are again separated from their solutions by acids (even CO₂). The addition of concentrated caustic alkali causes the colors to disappear. On diluting with water, the colors reappear.

To show the similarity of the phthaleins to the aurines or rosanilines in the formula, it is assumed that the free, colorless phthaleins contain the lactone ring; in their colored alkali salt solutions this ring is absent, and the methane carbon atom and an oxygen atom form a quinone-like union with a benzene nucleus. This idea is apparently supported by the preparation of phthaleinoxime:

$$C_6H_4\left\{\begin{bmatrix}1\\1\\2\end{bmatrix}CCC_6H_4\cdot OH\\Free\ Phenolphthalein \end{bmatrix}C_6H_4\left\{\begin{bmatrix}1\\2\\2\end{bmatrix}CO_2H\right\}OH\\C_6H_4\left\{\begin{bmatrix}1\\2\\2\end{bmatrix}CO_2H\right\}OH\\Phenolphthalein\ in\ Colored\ Alkali\ Salts.$$

It should also be added that lactone esters and ethers have also been obtained by acidylation and alkylization of phenolphthalein in alkaline solution (B. 28, 3258; 29, 131; compare B. 29, R. 552).

The phenolphthaleins, by reduction, yield oxytriphenylmethane carboxylic acids—the phthalins (p. 361). The latter are changed by concentrated sulphuric acid into oxyphenylanthranol derivatives, called phthalidines. The oxidation of the latter produces the phthalideines, or oxyphenyloxanthranol derivatives. The following diagram represents these changes, with phenolphthalein as the example:

$$C_{6}H_{4}\begin{cases} [1]_{C} & C_{6}H_{4}OH & C_{6}H_{4}OH & C_{6}H_{4}OH \\ [2]_{COO} & \pm 2H \end{cases} \xrightarrow{C_{6}H_{4}OH} \xrightarrow{C_{6$$

Phthalein Phthalldin, Phthalin, p_rDioxydiphenyl-phthalide p₂-Dioxytriphenyl-methane-o-carboxylic Acid Dioxyphenyl-anthranol Dioxyphenyl-oxanthranol.

Phenolphthalein, p₂. Phthalein, Dioxydiphenyl phthalide, C₃₀H₁₄O₄, is a yellow powder, crystallizing from alcohol in colorless crusts, and melting at 250°. It dissolves in the alkalies with a red color. It is used as an indicator in alkalimetry, especially in determining carbon dioxide with baryta (B. 17, 1907). It is formed from phthalophenone when nitrous acid acts on the p-diamido compound; by oxidizing an alkaline solution of the corresponding to the corr responding phthalin with air, or with potassium ferricyanide or potassium permanganate, and is also obtained on heating phthalic anhydride with phenol and tin chloride, or with substantial obtained on heating phthalic anhydride with phenol and tin chloride, or with sulphuric acid to 115-120° for eight hours. o. Dioxydiphenylphthalide anhydride,

insoluble in caustic potash, is a by-product. Boiling caustic potash and zinc-dust reduce phthalein to phthalin (p. 361), and it is decomposed into p₂-dioxybenzophenone and benpathalein to phthalin (p. 361), and it is decomposed into p_1 -dioxydenizophenole and the solic acid by fusion with caustic potash (A. 202, 68).

Lactone Derivatives of Phenolphthalein: Diacetophenolphthalein melts at 143°. Dibenzoylphenolphthalein melts at 169° (B. 29, 131). Dimethyl Phenolphthalein, melting at 98° (B. 29, 138, R. 848), has also been obtained synthetically phthalic anhydride, anisol, and Al₂Cl₆ (B. 29, R. 550). Phenolphthalein Anilide, C_6H_4 [I]C = $(C_6H_4 \cdot OH)_2$, melts at 279° (B. 26, 3077). Tetrabromphenolphthalein, $C_{20}H_{10}Br_4O_4$, melts with decomposition at 220–230°. In the colored alkali salts are quinoid derivatives of phenolphthalein.

The colored alkali salts are quinoid derivatives of phenolphthalein. In this classical salts are quinoid derivatives of phenolphthalein. In this class is also—

Phenolphthale in Oxime, C_6H_4 $\begin{cases} [1]C & C_6H_4 \cdot OH \\ C_6H_4 = N \cdot OH \end{cases}$, a yellow crystalline powers.

der, melting with decomposition at 221°, and produced by the action of hydroxylamine upon an alkaline phenolphthalein solution. Boiling, dilute sulphuric acid decomposes the oxime into p-oxy-o-benzoylbenzoic acid and p-amidophenol (B. 26, 172). Tetra-bromphthalein Oxime (B. 26, 2260). See B. 30, 176, upon the quinoid tetrabromphenolphthaleinmono- and -diethyl ethers.

Fluorane, o₂. Phenolphthalein Anhydride, C₆H₄[2] O C

173-175°, is produced, together with p₃-phenolphthalein, by the condensation of phthalic anhydride and phenol. Fluorane yields hydrofluoranic acid by reduction (p. 362), and diphenylenephenylenethane when it is distilled over zinc-dust (B. 25, 3586). The anil,

 $\int [1] \dot{C} = (C_6 H_4)_2 O$, melts at 242° (B. 27, 2793). Tribromfluorane, CmII, [2]CON. C₆H₅
Br₁O₅, melting at 298-300°, is produced by the action of PBr₅ upon fluoresceIn, and is

reduced by alcoholic caustic soda and zinc-dust to hydrofluoranic acid (B. 25, 1388).

The fluoresceins are the o-phthalic anhydrides produced by the condensation of phthalic anhydrides with resorcinol. They are characterized by a beautiful fluorescence; this is especially true of their alkaline solutions (Baeyer, A. 183, 1).

Phthalic anhydride may also be replaced by the anhydrides of aliphatic When succinic, maleic, and citraconic anhydrides dicarboxylic acids. are condensed with resorcinol, the corresponding fluoresceins are produced. See also naphthalic acid (B. 15, 883; 18, 2864; 24, R. 763; 26, R. 542; 29, 2824).

Resorcinol-phthalein, Fluorescein, C₂₀H₁₂O₅, is prepared by heating phthalic anhydride (2 parts) with resorcinol (7 parts) to 200°, or with anhydrous oxalic acid (B. 17, 1079) to 110-117°. When precipitated from its salts it is a yellowish-red powder, C₂₀H₁₄O₆, which quickly loses water and becomes C₂₀H₁₃O₅, which dissolves in alcohol with a yellowred color and green fluorescence. Its concentrated alkali solution is dark red, but on dilution it gradually becomes yellow, and then exhibits a magnificent yellowish-green fluorescence. Upon reduction fluorescein yields fluorescine (p. 362), and PCl₆ converts it into fluorescein chloride, p₁-dichlorfluorane (see rhodamines, p. 366 (A. 183, 18).

Bacyer asseribes the formula C_0H_4 $\begin{cases} [1]C = (C_0H_2OH)_2O \\ [2]COO \end{cases}$ s a disposition to assume that the to fluorescein.

was a disposition to assume that the phthalic acid residue replaced both m-hydrogen atoms (5) in the resorcinol molecules, R. Meyer showed that fluorescein is a dioxyderivative of o-phenolphthalein anhydride, for which reason he gave it the name fluorane (above); that, therefore, the phthalic acid residue occupied the o-position with reference at least to each of the hydroxyl groups of the resorcinol molecule, and between these hydroxyl groups the anhydride formation occurred. R. Meyer converted fluorescein (1) by means of PBr, into tribromfluorane (2), which, like fluorane (4) itself, yields hydrofluoranic acid (3) upon reduction. Fluorescein and fluorane contain a ring closely related to the xanthone ring; indeed, hydrofluoranic acid (p. 362) may be decomposed into xanthone and benzene:

$$\begin{array}{c} \text{(1)} \\ \text{C}_{\mathbf{g}}\text{H}_{4} \\ \\ \text{[2]Coo} \end{array} \\ \begin{bmatrix} \text{1]}\text{C} < \begin{matrix} C_{\mathbf{g}}\text{H}_{3}(\text{OH}) \\ C_{\mathbf{g}}\text{H}_{4}(\text{OH}) \\ 2 \end{matrix} \\ \\ \text{2} \end{bmatrix} \\ \begin{array}{c} \text{O} \\ \text{(2)} \\ \text{(2)} \\ \text{(2)} \\ \text{(3)} \\ \text{(2)} \\ \text{(3)} \\ \text{(4)} \\ \text{(1)}\text{(1)} \\ \text{(2)} \\ \text{(2)} \\ \text{(2)} \\ \text{(3)} \\ \text{(3)} \\ \text{(2)} \\ \text{(2)} \\ \text{(3)} \\ \text{(3)} \\ \text{(4)} \\ \text{(1)}\text{(1)} \\ \text{(2)} \\ \text{(2)} \\ \text{(3)} \\ \text{(2)} \\ \text{(3)} \\ \text{(3)} \\ \text{(4)} \\ \text{(4)} \\ \text{(1)}\text{(2)} \\ \text{(2)} \\ \text{(2)} \\ \text{(3)} \\ \text{(4)} \\ \text{(4)} \\ \text{(4)} \\ \text{(5)} \\ \text{(6)} \\ \text{(6$$

The stense refer of fluorescein led Bernthsen and others to ascribe a quinoid consistence of creecein and its colored derivatives (see phenolphthalein). The colorles of the were supposed to have their origin in the lactone formula of fluorescein. This is a self-consistent and its colored derivatives with the aurines and rosanilines.

A restriction is fused with caustic soda it breaks down into resorcinol and monomical in or dioxylenzoylbenzoic acid. Bromine in glacial acetic acid to be interested dibromedioxybenzoylbenzoic acid, which furning sulphuric acid to a restriction in remaining urpurine: it is also obtained from eosin. Hence it follows that the restriction is acid it would be impossible for an anthraquinone condensation with the second state of the second seco

ite et. B 28, 314, B, 29, 2623).

Fluorescein Anilide, C₂₀H₁₇NO₄. The inthe colorless, melts at 207°, and when boiled with sulphuric acid changes to

... fluorescein dimethyl ether, melting at 198° (B 28, 390).

Fluorescein Carboxyl Ethyl Ether, melting at 196° (p. 362), which is the oxidation of fluorescein ethyl ether, melting at 196° (p. 362), which is the oxidation of fluorescein ethyl ether, melting at 196° (p. 362), which is the carboxyl ethyl ether into the colored diethyl ether, melting at 159°. This is the lark yellow needles. The dimethyl ether, melting at 208°, is made from the result by the action of methyl alcoholic potash and methyl iodide (B. 28, 396; b. 29, R. 848).

She remainst Fine recorders.—Although fluorescelle itself is not applicable as a dye, by the lucing halogens and nitro-groups into it dyestuffs of remarkable beauty can be obtained. If we start with fluorescelle, then the substitution will occur in the resorting

: - lacs.

It bromine be allowed to act on fluorescein suspended in glacial acetic acid, Eosin, Tetrabromfluorescein, $C_{11}H_1B_1O_2$, is produced. Crystallized from alcohol it forms a law state. The cost invariant satisfaction sailts constitute the eosin of commerce, soluble on water, at I imparting to wool and silk a beautiful rose-color. In the case of the salit must there is a yellowish-red fluorescence (Caro, 1873).

Erythrosine, Ten il dilucrescin, C20H, I4O5.

Safrosine, F. on S. o. f. Dibroundinitrofluorescein, C₂₀H₂Br₂(NO₂)₂O₅, is formed when became acts upon dinitrofluorescein, or when nitric acid acts upon disor tetratrombusescein (A. 202, 68). See B. 30, 333, for the dinitrofluorescein yellow from dinitrofluorescein and ammonia.

To obtain the thioresceins substituted in the phthalic acid residue, condense the chlorinated phthalic anhydrides with resorcinol (Noelting). The brom- and iodifluoresceins with the substituents in the resorcinol residues, are at the same time prepared from the chlorinated bodies:

Phlorine, Tetrabromdicklor, and Tetrabromtetrachlorfluorescein, CooH4Cl4Bt(0)

Rose Bengal, Tetraiodtetra klorthorescein.

Phthalic anhydride has also been condensed with pyrocatechol (B. 22, 2107), history

quinones, ordins, and phloroglucin.

Pyrogallol-phthaleïn, Galleïn, $C_{20}H_{10}O_7$, is obtained on heating pyrogallic acid with phthalic anhydride to 200°. It forms crystals with green color, dissolving with a dark red color in alcohol and with a beautiful blue color in the alkalies.

It is converted by concentrated sulphuric acid into Coerulein (see A. 209, 240).

The rhodamines, the phthaleins of m amidophenol and its derivatives, are of special importance. They are violet red, magnificently fluorescent dyestuffs. In constitution they are perfectly analogous to the fluoresceins.

The *simplest* rhodamine is formed when m-amidophenol hydrochloride and phthalic anhydride are heated to 100° with concentrated sulphuric acid (B. 21, R. 682).

The alkylic rhodamines possess more intense colors. They are produced when rhodamine hydrochloride is heated with alkyl iodides. A better course to pursue is the condensation of alkylic manidophenols and phenyl-manidophenol with phthalic anhydride (B. 21, R. 082, 020; 22, R. 788). Still another procedure consists in rearranging fluorescein chloride, melting at 252° (the product of the action of PCl₃ upon fluorescein) by heating it with dialkylamines (B. 22, R. 625, 789).

Anisolines, alkyl ethers of the rhodamines (21-see B 25, R. 806.

Succino-rhodamine has been obtained from succinic anhydride and m-amidophenol (B. 23, R. 532).

All that has been said relative to the constitution of the fluoresceIns applies to the rhodamines. The nomenclature of the fluoresceIns can be greatly simplified if the bodies having the atomic group $-C \begin{pmatrix} C_8H_4 \\ C_6H_3 = O \end{pmatrix}$ are designated fluorones, and those

with the atomic group $-C < C_8H_4 > 0$, fluorimes (B. 27, 2987). $C_8H_3 = NH$

Consult B. 28, 2959, for the ordin phthaleins and hydroquinone phthaleins. Hydroquinone phthalein does not behave like fluorescein, hence probably does not contain the fluorane residue which is present in the latter compound. The condensation of phthalein anhydride with ordinol and sulphuric acid or P₂O₈ gives rise to three ordinol phthaleins. It is only that ordinol phthalein, however, which contains the two hydroxyl groups in the p-position with reference to the phthalic acid residue which is the perfect analogue of fluorescein (B. 29, 2630).

IV. DIPHENYL ETHANE GROUP.

Homologous series are derived from diphenylmethane. Dismissing the substitutions in the benzene residues, this is attained by replacing the H-atoms of the methylene residue by alkyl groups: diphenylmethyl-, diphenyldimethyl-, diphenylpropylmethane, etc.; and, again, it can be done by inserting new C-atoms between the two benzene residues: ω, ω -diphenyl ethane or dibenzyl, ω, ω -diphenyl propane, ω, ω -diphenyl butane, ω, ω -diphenyl pentane, etc. A sharp division is impossible, because of the unequal experimental investigation of the material. The group of unsym. diphenylethane or diphenylmethylmethane will receive first attention in the following paragraphs; its members attach themselves in their deportment to diphenylmethane and its derivatives; at the same time they show in many ways their genetic relationship to the dibenzyl group. Compare benzilic acid, diphenylacetaldehyde, stilbene, tolane.

After these there will follow the important dibenzyl or sym. diphenylethane group, and then the ω, ω -diphenyl-, propane-, butane-, pentane-, and hexane-groups. The derivatives alkylized or phenylated in the benzene nuclei, or in the side-chains connecting these, are included with the parent hydrocarbons of the individual groups; the saturated are followed by the unsaturated hydrocarbons.

A. Unsym. Diphenyl Ethane Derivatives are, as a rule, formed by the condensation of aldehyde, chlorinated aldehydes, glyoxylic scid, etc., with benzene hydrocarbons, phenols, or tertiary anilines, just as the diphenylmethanes (p. 342) are produced by means of methylal, methylene iodide, etc.:

$$CH_3$$
. $CHO + 2C_6H_6 \longrightarrow CH_3CH(C_6H_6)_2 + H_2O$.

All the substances included in this class yield benzophenone or its derivatives when they are oxidized.

Unsym. Diphenyl Ethane, $(C_0H_5)_2$ CHCH₃, boiling at 209° (145° at 13 mm.), is made from benzene and paraldehyde with cold sulphuric acid; also from ethidene chloride, CH₂CHCl₃, sym. brom-ethyl benzene, C_0H_5 . CHBr. CHI₃, or styrene with benzene and Al₂Cl₃. Chromic acid oxidizes it to benzophenone, with the elimination of the methyl group. Consult B. 27, 2338. Nitric acid nitrates the side-chains and not the

benzene residues of unsym. diphenyl-ethane. The products are: Diphenylethylene glycol mononitrite, $(C_4H_5)_3C(OH)$. $CH_2(ONO)$, melting at 100°, diphenylvinyl nitrite, $(C_4H_5)_3C=CH(ONO)$, melting at 86°, and a dinitrite melting at 148-149°. The latter is probably a diphenyl-ethylene derivative. These three compounds have great crystallizing power. They form yellow crystals, and when oxidized yield benso-

phenone (A. 233, 330).
Unsym. Phenol Phenylethane, C₈H₈CH(CH₂)C₈H₄. OH, melting at 58°, is produced when sulphuric acid acts upon phenol and styrene; the homologous phenols, naphthols, etc., behave similarly toward styrol (B. 24, 3891). Unsym. diphenolethane, (CaH4OH), CHCH3, melting at 122°, can be obtained from aldehyde and phenol (B.

19, 3009).

Unsym. Diphenyl Monochlor-ethane, (C₆H₅)₂CH. CH₂Cl, is an oil. Diphenyl Dichlor-ethane, (C₆H₅)₂CH. CHCl₂, melting at 80°, and Diphenyl Trichlor-ethane, (C₆H₅)₂CH. CCl₃, melting at 64°, are obtained from mono, di., and trichlor-acetaldehyde (chloral) with benzene and sulphuric acid. Alkali, acting upon these sub-

stances, splits off hydrogen chloride, and the products are:

unsym. Diphenyl Ethylene, $(C_8H_6)_2CH: CH_2$, melting at 44° and boiling at 277°, which can also be formed from unsym. dibromethylene, $CBr_2: CH_2$, with benzene and $Al_1Cl_4:$ diphenylmonochlor-ethylene, $(C_8H_6)_2C: CHCl$, melting at 42° and boiling at 298°, and diphenyldichlorethylene, $(C_8H_6)_2C: CCl_2$, melting at 80° and boiling at 316°, which is also found in the condensation products of chloral with benzene and aluminium chloride (B. 26, 1955). If diphenylmonochlor-ethane be heated alone it splits with hydrochloric acid and is rearranged to still be a_1 (B. 26). The letter is similarly off hydrochloric acid and is rearranged to stilbene (p. 369). The latter is similarly produced by the reduction and rearrangement of diphenyltrichlorlethane with zinc-dust and alcohol. When diphenylmonochlor-ethylene is heated with a sodium ethylate solution it is transformed into tolane (p. 370). Diphenylvinyl Ethyl Ether, (CaHc), C:-CHOC, H5, is formed simultaneously:

$$(C_6H_5)CH \cdot CH_2CI \xrightarrow{-HCI} C_6H_5 \cdot CH : CH \cdot C_6H_5$$

 $(C_6H_5)_2CH : CHCI \xrightarrow{-HCI} C_6H_5 \cdot C : C \cdot C_6H_5$

These transposition reactions have been extended to a series of substituted diphenylmono and trichlor-ethanes and to diphenylmonochlorethylene (A. 279, 319; B. 26, R.

When diphenylvinyl ether is saponified with glacial acetic acid and hydrochloric acid it does not yield diphenylvinyl alcohol, but diphenylacetaldehyde, (CaH5)2CH CHO, boiling at 168-172° (28 mm.). The oxime melts at 120°. The aldehyde in many respects deports itself analogously to the oxymethylene derivatives -e. g., when it is oxidized it does not change to the acid, but splits off the CHO-group and becomes benzophenone (B. 24, 1780; 25, 1781). Diphenylacetaldehyde is also formed from the hydrobenzoins by dehydrating agents. Anhydrides of the hydrobenzoins are formed at the same time:

$$C_8H_5$$
. CH. OH. CH. OHC₈ $H_5 \xrightarrow{-H_8O} (C_8H_5)_9$ CH. CHO.

This is due to an atomic rearrangement opposite to that of the transpositions of the unsym. diphenylchlor-ethanes and ethylenes just indicated. It reminds one of the

pinacoline rearrangement of the pinacones.

Diphenyl Acetic Acid, (C₆H₅)₂CH. CO₂H, is formed from its cyanide; and by reducing benzilic acid with hydriodic acid and phosphorus in glacial acetic acid (A. 275. 84). The acid melts at 146°. When oxidized with a chromic acid mixture it yields benzophenone; and when heated with soda lime we get diphenyl methane. Its ethyl ester

melts at 58°; the methyl ester at 60°.

Diphenylacetonitrile, (C₈H₃)₂CH. CN, results when diphenylbrommethane is heated with Hg(CN)₂, or by the condensation of mandelic nitrile, C₈H₅. CH(OH)CN, and benzene with tin tetrachloride (B. 25, 1615). It melts at 72° and boils at 184° (at 12 mm.). The hydrogen of its CH-group is readily replaced by the benzene residue. but not by alkyls (A. 275, 87). Iodine, acting upon its sodium derivatives, produces tetraphenyl-succino nitrile.

Tetranitro-diphenyl Acetic Acid, $C_6H_3(NO_2)_2 > CH \cdot CO_2H$.

The ethyl ester is derived from dinitro-phenyl-acetoacetic ester and dinitro-phenylmalonic ester (pp. 258, 259) by the action of 0,p-dinitrobrombenzene; the group CO. CH₃ (and CO₃. C₃H₄) being replaced. It may be similarly prepared from dinitro-phenylacetic ester by the introduction of the dinitro-phenyl residue. It melts at 154°. Alcoholic potash or soda converts the ester, by the substitution of the hydrogen of the CHgroup, into brilliant metallic salts, dissolving in alcohol and water, with a dark blue color. Compare tetranitro-phenylmethane, [(C₈H₃NO₃)₂]CH₂ (p. 343) and trinitrotriphenyl methane (C₈H₄NO₃)₃CH (p. 352) (B. 22, 2476).

The lactone of a tetraoxydiphenylacetic acid, COOH. CH[C₈H₃(OH)₂]₃, has been

obtained by the condensation of chloral with resorcinol by means of potassium bisulphate. It has a yellow color. It dissolves in cold alkalies with a red color, and forms

a triacetyl derivative, melting at 152° (B. 29, R. 776).

Benzilic Acid, Diphenyl Glycollic Acid, (C₆H₅)₂C(OH). CO₂H, melting at 150°, is produced by a molecular rearrangement of benzil (see this) when digested with alcoholic potassium hydroxide, and from diphenyl acetic acid by the action of bromine and boiling with water. We can prepare it better by the action of aqueous potash and air upon benzoln (B. 19, 1868).

$$C_aH_5$$
. CO. CO. $C_aH_5 \xrightarrow{H_2O} (C_aH_5)_2C(OH)COOH$.

When heated above its melting point benzilic acid takes on a blood-red color and dis-solves with the same color in sulphuric acid. Diphenylenediphenylethane derivatives are produced by the action of concentrated sulphuric acid upon benzilic acid (B. 29, 734). It yields diphenyl acetic acid when heated with hydriodic acid and phosphorus. On distilling its barium salt it breaks up into carbon dioxide and benzhydrol; oxidation yields benzophenone.

Anisilic Acid, (CH₂OC₆H₄)₂C(OH)COOH, Cuminilic Acid, (C₂H₁C₆H₄)₂C(OH)COOH, and Ilexamethoxybenzilic Acid, [(CH₃O)₃C₆H₂]₂C(OH)COOH, are prepared,

like benzilic acid, from their corresponding substituted benzils (p. 375).

\$\beta_{\beta}\$ Diphenyl Propionic Acid, (C_6 \text{II}_6)_2 CH. CH_2. COOH, is a homologue of diphenylacetic acid. It melts at 149°. It is formed by the addition of benzene to cinnamic acid. This is accomplished by means of sulphuric acid, just as phenol-phenylethane is obtained from styrol and phenol (p. 368). The continued action of the sulphuric acid leads to a condensation to γ -phenylhydrindone (p. 387). Phenyltolyl-, phenylxylyl-propionic acids, etc., are prepared just like diphenylpropionic acid (B. 26, 1579). Potassium permanganate oxidizes these acids to benzophenone, phenyltolylketone, phenylxylylketone, etc.

y-Diphenylitaconic Acid, (C₆H₅)₂C: C(COOH). CH₂. COOH, is obtained by the condensation of benzophenone with succinic ester through the agency of sodium ethylate

Triphenyl Acetic Acid, (C₆H₅)₃C. COOH, is a very feeble acid. It melts at 264° and decomposes into triphenylmethane and carbon dioxide. It is isomeric with the previously described triphenylmethane carboxylic acids. It is made by the action of benzene and aluminium chloride upon trichloracetic acid, and when carbon dioxide is conducted over potassium triphenylmethane (p. 357) at 200°. The best procedure consists in using the nitrile, (CoHo)3C.CN, melting at 127°; the latter is produced by the interaction of triphenylchlor or brom methane (p. 353) and mercuric cyanide, IIg(CN), (A. 194, 260; B. 28, 2782), or by deamidizing hydrocyanpararosaniline (B. 26, 2225).

p. Triamido-triphenyl-acetic Nitrile, Hydrocyanpararosaniline, results upon di-

gesting pararosaniline salts with alcohol and potassium cyanide. Hydrocyanrosaniline is similarly obtained from the rosaniline salts. The hydrochlorides of these hydrocyanbodies break down under the influence of heat into HCl, HCN, and the salts of

B. Sym. Diphenylethane Group: Dibenzyl, sym. Diphenylethane, CaH5. CH2. CH₂. C₂H₅, melting at 52° and boiling at 284°, is prepared (1) by the action of sodium or (copper) upon benzyl chloride, C_8H_5 . CH_2Cl , or (2) of AlCl, upon benzene and ethylene chloride or ω -chlorethyl benzene (A. 235, 155), and (3) by heating benzoln, stilbene, and tolane with hydriodic acid. It forms stilbene and tolane when heated to 500°. Chromic acid and potassium permanganate oxidize it directly to benzoic acid. It yields two dinitro compounds by nitration.

p,p Dinitrodibenzyl has also been obtained by the action of stannous chloride upon

p nitrobenzyl chloride. It melts at 179° (A. 238, 272; B. 20, 909).

Dibenzyl Homologues: a,β -Phenyltolylpropane, $C_0H_0CH_1CH_2$, and a,β -Phenylxylylpropane, are produced when concentrated sulphuric acid acts upon styrol in the presence of xylene or trimethylbenzene. The homologous benzenes, containing a methyl group, attach themselves to the unsaturated linkage in the styrol (B. 23, 3269).

Diphenyldimethyl Ethane, C_6H_5 . CH(CH₃)CH(CH₃)C₆H₅, melting at 123°, is formed when sodium or zinc-dust acts upon a β -haloid ethyl-

benzene, C₆H₅. CHX. CH₃ (B. 26, 1710).

Stilbene, Toluylene, sym. Diphenyl-ethylene, C_6H_5 . CH: CH: C_6H_6 , melting at 124° and boiling at 306°, crystallizes in large, glistening $(\sigma \tau i \lambda \beta \epsilon \nu)$, to glisten) monoclinic leaflets or prisms. It is obtained by a great variety of methods. It belongs to a long-known class of aromatic substances (Laurent, 1844). It is produced:

(1) By distilling benzyl sulphide and disulphide;

(2) By heating polymeric thiobenzaldehyde (p. 185) to 150°, or by distilling trithiobenzaldehyde with metallic copper (B. 25, 600);

(3) By the action of metallic sodium upon benzaldehyde or benzal

chloride;

(4) From chlorinated, asymmetrical diphenyl ethane derivatives—e.g., (C₆H₅)₂CH . CH₂Cl (p. 368), (C₆H₅)₂CH . CCl₃, by a rearrangement caused by heat or zinc-dust (B. 7, 1409; J. pr. Ch. [2], 42, 44);

(5) By the action of metallic copper, potassium sulphydrate (B. 24,

1776), or potassium cyanide (B. 11, 1219) upon stilbene dihalides.

(6) An interesting method for its production is that of distilling fumaric and cinnamic phenyl esters (B. 18, 1945):

When heated with hydriodic acid stilbene yields dibenzyl. The addition of halogens produces stilbene dihaloids, the haloid esters of the hydrobenzolns (p. 371). Chromic acid oxidizes stilbene to benzaldehyde and benzoic acid. Thionessal, tetraphenylthiophene (see this), is produced when stilbene is heated for several hours at 250°, together with sulphur. Phenanthrene is formed when stilbene is heated.

Stilbenes having the substituents in the benzene nucleus are obtained from substituted benzyl- and benzal-chlorides; thus, o-chlorbenzal chloride and copper yield 0.0 Dichlorstilbene, (Cl. C₆II₄. CII)₂, melting at 97°, and chlornitrobenzyl chloride and alcoholic potash give rise to Dichlornitrostilbene, melting at 294° (B. 25, 79; 26, 640).

The action of alcoholic potash upon o- and p-nitrobenzyl chlorides gives rise to two physical isomerides in each case: two 0,0-Dinitrostilbenes, melting at 126° and 196° respectively, and two p.p-Dinitrostilbenes, melting at 210-216° and 280-284° (B. 21, 2072; 23, 1959; 26, 2232), which yield corresponding diamidostilbenes upon reduction. 0₂-Diamido-stilbene, (cis-) melting at 123° and (trans-) at 168°, changes to indol (good yield) on heating equivalent quantities of the hydrochloride and base; aniline is eliminated (B. 28, 1411). The disulphonic acid of p₂-diamido-stilbene (melting at 227°), by diazotizing and combining with phenol, passes into a tetrazo-compound, brilliant yellow.

CH. C₆II₃(SO₃H)N: NC₆II₄OH

The mono-ethyl derivative, \parallel CH . $C_6\Pi_3(SO_3H)N:NC_6\Pi_4O\Pi$, of the latter is the substantive cotton-dye, chrysophenine (B. 27, 3357).

See B. 22, R. 311 (compare benzidine dyes, p. 338), for additional dye-substances. o,o-Dioxystilbene, melting at 92°, is produced, together with other bodies, on boiling salicylaldehyde with zinc-dust and glacial acetic acid (B. 24, 3175).

Tolane, Diphenyl Acetylene, C₆H₅. C : C. C₆H₅, melting at 60°, is produced from stilbene bromide on boiling with alcoholic potash, and, further, together with diphenylvinyl ether (p. 368), on treating unsym. diphenylchlor-ethylene, (C₆H₅)₂C: CHCl, with sodium alcoholate.

The latter method proceeds more smoothly with the substituted tolanes. Dimethyl Tolane, melting at 136°, and dimethoxytolane, melting at 145°, are obtained from ditolyl- and dianisylchlorethylene. o,o-Dichlortolane, melting at 89°, is made from o,o-dichlorstilbene dichloride.

The tolanes absorb two and four halogen atoms, the products being tolane di- and tetra-chlorides (see these). The elements of water are taken up by the action of glacial acetic acid and sulphuric acid, with the formation of desoxybenzoins (below) (compare vol. 1, p. 96).

1. Alcohol and Ketone Derivatives of Dibenzyl:

C₆H₆CO C₆H₆. CH.OH C₆H₆. CO C₆H₆. CH₂ C₆H₆. CH.OH C₆H₆. CH.OH C_aH_a. CH. OH C.H. CH. Hydrobenzoin Stilbene Hydrate

Stilbene Hydrate, Toluylene Hydrate, C6H5. CH(OH). CH2. C6H5, melting at

62°, results upon reducing desoxybenzoin with sodium amalgam.

Desoxybenzoin, *Phenyl-benzyl ketone*, C₆H₅. CO. CH₂. C₆H₅, melting at 60° and boiling at 314°. It is obtained (1) by distilling a mixture of calcium benzoate and calcium a-toluate; (2) when AlCl₃ acts upon a mixture of alphatoluic chloride; (3) by reducing benzoin with zinc and hydrochloric acid (B. 21, 1296); (4) from chlorobenzil and benzil (B. 26, R. 585) by the action of hydriodic acid; (5) by heating monobrom-toluylene with water to 180-190°. One H-atom of its CH₂-group can be replaced Jy sodium and alkyls, but not the second (B. 21, 1297; 23, 2072). Methyl-, isobutyl-, cetyl-desoxybenzoin melt at 58°, 78°, and 76° (B. 25, 2237).

Its oxime melts at 98°. Isonitrosodesoxybenzoin, produced by N₂O₃, is identical with

a benzil monoxime (p. 373). Hydriodic acid converts desoxybenzoln into dibenzyl-

see also stilbene hydrate.

The nitration of desoxybenzoin produces o-nitrodesoxybenzoin, C₈H₄(NO₂)CH₂. CO. C. H., which, upon reduction, yields a-phenyl-indol, C. II. CH NH C. C. H. Des-

oxytoluoin, CH₃. C₆H₄. CH₂. CO. C₆H₄. CH₃, and Desoxyanisoin, CH₃O. C₆H₄. CH₂. CO. C₆H₄. OCH₃, are formed from the corresponding tolanes (A. 279, 335, 339) (above). CSCl₃, or carbon disulphide, and caustic potash, convert the desoxybenzoins into desaurines, which form brilliant golden-yellow needles. They dissolve in sulphuric acid with a violet-blue color. The exact constitution of these bodies is not yet known. The simplest desaurine very probably has the composition CaHaCOC(CS)CaHa (B. 25, 1731, 2239).

Hydrobenzoin, Toluylene Glycol, C₆H₅. CH(OH)CH(OH)C₆H₅, has two asymmetric C-atoms and occurs in two optically inactive modifications (A. 259, 100): hydrobenzoin, melting at 134°, and isohydrobenzoin, melting at 111°. The latter has been resolved into two optically active components (see below). Both are produced, together with benzyl alcohol, when zinc and alcoholic hydrochloric acid act upon oil of almonds, or when the latter is treated with sodium amalgam, or in the electrolytic reduction of tenzaldehyde (B. 29, R. 229). Both are also obtained from stilbene bromide or chloride on converting the latter by silver acetate or benzoate into esters, and saponifying these with alcoholic ammonia. With potassium acetate, isohydrobenzoin is almost the sole product. HydrobenzoIn predominates (with a little isohydrobenzoIn) when sodium amalgam acts on benzoIn. This is also the best method for its preparation (A. 248, 36). Hydrobenzoin dissolves with difficulty in water, crystallizes in rhombic plates, melting at 134°, and sublimes without decomposition. The diacetate is obtained from benzaldelyde and acetyl chloride by means of zinc-dust (B. 16, 636); it melts at 134°.

Isohydrobenzoin is more readily soluble in water. It crystallizes in prisms which

contain water of crystallization and rapidly effloresce on exposure. Its discrete is dimorphous, and crystallizes in shining leaflets, melting at 118°, or in rhombic prises melting at 106°.

C₆H₅CH.O.CH.C₆H₆
Dimolecular anhydrides, C₆H₅.CH.O.CH.C₆H₆
Obtained, together with diphenylacetaled hyde, (C₆H₅)₂CH. CHO, from both hydrobes-

voins by the action of sulphuric acid or $P_2(t)_2$.

By crystallization from ether isohydrobenzoin has been resolved into enantiomorphous dextro- and lavo-rotatory crystals (B. 30, 1531). Chromic acid or potassium permangnate changes both hydrobenzoins into benzaldehydes, and nitric acid converts them into benzoin (B. 24, 1776). PBr₅ changes both to the same stilbene dibromide, C₄H₅. CHBr. CHBr. C₆H₅, melting at 237°, which has also been made by the action of bromine upon stilbene and dibenzyl. Stilbene and bromine yield not only the body (the a) melting at 237°, but also a β-variety, melting at 110°. This is more readily soluble. It passes into the higher-melting variety under the influence of heat, and this again reverts by alcoholic potash into *liquid* monobromstilbene, whereas the β -modification by similar treatment changes to a *solid* monobromstilbene (p. 375) (B. 28, 2693). Both hydrotenzoins are changed by PCl₅ into a- and β -Stilbene Dichloride, melting at 192° and 93°. The a-compound is also produced when chlorine acts upon stilbene dissolved in chlore-

form. When heated to 200° the β-passes into the a-variety.

Diphenyloxethylamine, C₄H₅. CH(OH)CH(NH₂)C₄H₅, melting at 161°, and isodiphenyloxethylamine, melting at 128°, are produced together by the reduction of benzoinoxime, and also from the condensation products of glycocoll with benzaldehyde, as well as from benzaldehyde and benzylamine by the action of sodium hydroxide. N₂O₃ converts isodiphenyloxyethylamine into isohydrobenzoln (B. 28, 1866, 2524; 29, 295; 30, 1527). Diphenyl-ethylene-diamine, Stilbene Diamine, CellscH(NH₂)CH(NH₂)CH₂, melting at 91°, is produced by reducing benzil dioxime with sodium and It is resolved by crystallization of its bitartrate into two optically active comalcohol,

ponents (B. 28, 3167).

The diesoanhydride of an 0,0-dioxyhydrobenzoin, O. CaH4. CH. CH. CaH40, has been obtained in two modifications, melting at 68° and 114°, by the reduction of salicylaldehyde with zinc-dust and glacial acetic acid.

Benzoin, w Benzyl Alcohol Phenyl Ketone, melting at 134°, C.H. CH(OH). CO. C₆H₅, is produced when the hydrobenzoins are oxidized with concentrated nitric acid, and by the condensation of two molecules of benzaldehyde with potassium cyanide in aqueous-alcoholic solution.

This reaction is also shown by other aromatic aldehydes (see B. 25, 293; 26, 60). The products are ketone alcohols,—e.g., anisom, CH₃O. C₂H₄CH(OH)CO. C₄H₄COCH₃: Cuminom, etc., from anisic aldehyde, cuminol (see also furfurol, phenylement) glyoxal),—and reduce Fehling's solution, being at the same time oxidized to the corresponding benzils.

Chromic acid oxidizes benzoin to benzaldehyde and benzoic acid, while nitric acid changes it to benzil; nascent hydrogen reduces it to hydrobenzoin. The latter and benzil are produced when benzoin is boiled with alcoholic potash. If air be simultane ously introduced, benzil is the chief product, and it is further changed to benzilic acid (p. 369).

Benzoin Hydrazone melts at 75° (J. pr. Ch. [2], 52, 124). at 158° and 106° (B. 28, R. 788). The oxime melts at 152°. The phenylhydrazones melt Alcohols and hydrochloric acid alkylize benzoin: methyl benzoin, CoH5CH(OCH3)COC6H5, melts at 50°, and ethyl

benzoin at 62° (B. 26, 2412).

The hydrobromic acid ester of benzoln—desylbromide, C₆H₆. CHBrCOC₆H₆, melting at 55°—is obtained from desoxybenzoln (see below) and bromine. Aniline converts it into desylanilide, bensolnanilide, C₈H₅CH(NHC₈H₅)CO. C₈H₅, melting at 99°, which is also produced when aniline is heated together with benzoln. When heated together with aniline hydrochloride to 160°, the product is benzoinanilanilide, CaH3CH(NH . -C₆H₆)C(NC₆H₆)C₆H₆, melting at 125°; and when with aniline and zinc chloride at still
NH . C₆H₄ (R. c. 7.26, 66.0)

higher temperatures: diphenylindol, $C_0H_5C = C \cdot C_0H_5$ (B. 26, 1336, 2640).

Benzoin-p-toluide, $C_0H_6CH(NHC_0H_4 \cdot CH_3)CO \cdot C_0H_5$, melting at 145°, is formed in the condensation of benzaldehyde with benzylidene toluidine by means of potassium cyanide (B. 29, 1736). o-Diamines and benzoin condense to dihydroquinoxalines; urea and thioureas with benzoin yield glyoxalines, while oxazoles are produced in the condensa-tion of benzoin with acid nitriles. For the condensation products of benzoin with acetone and acetophenone consult B. 26, 65, and p. 380.

Benzil, Dibenzoyl, Diphenylglyoxal, C₆H₅. CO. CO. C₆H₅, melting at 90° and boiling at 347°, consists of beautiful yellow prisms. It is the most easily obtained a-diketone. It is produced on boiling stilbene bromide with water and silver oxide and by digesting benzoin with concentrated nitric acid.

Benzil and hydrazine hydrate form hydrazibenzil, $C_6H_5C\left(\begin{smallmatrix}NH\\NH\end{smallmatrix}\right)CO$. C_6H_5 , and

$$\textbf{bishydrazibenzil}, \left[C_6 H_6 C \left({ {NH \atop NH} } \right) \right]_2, \text{which yield azobenzil}, C_6 H_6 C \left({ {N \atop N} } \right) \text{CO.C}_6 H_6$$

and bisazobenzil,
$$\left[C_0H_0\cdot C\left({\scriptsize \begin{array}{c} N\\N \end{array}} \right)\right]_2$$
, on oxidation (B. 29, 775). The osazone,

(C₆H₅)₂. C₂(NNH. C₆H₅)₂, melting at 225°, becomes triphenylosotriazole on heating (A. 232, 230; B. 26, R. 198). An isomeric modification of benzilosazone, melting at 208°, has been obtained by the action of iodine and sodium ethylate upon benzalphenylhydrazone. When heated above its melting point it changes to the higher melting modification (B. 29, R. 863).

One molecule of hydroxylamine, acting upon benzil, produces two isomeric monox-

imes, the a- melting at 134°, and the y- at 113°.

The former passes into the latter by heating it to 1000 with alcohol, or upon dissolving it in glacial acetic acid with hydrochloric acid. a-Monoxime and hydroxylamine form abenzil dioxime, while the y-monoxime yields y-benzil dioxime (B. 22, 540, 709). Compare B. 26, 792, R. 52, for their behavior with phenylhydrazine.

Both monoximes break down, upon heating, into benzonitrile and benzoic acid. deportment of the benzil monoximes in the Beckmann oxime rearrangement is very interesting. It is effected by means of PCl₅: a-monoxime yields benzoyl benzimide chloride, readily decomposing into benzonitrile and benzoyl chloride, while the γ -monoxime yields benzoylformic acid-anilide chloride:

In the first instance the hydroxyl exchanged positions with the phenyl residue, in the second with the benzoyl residue, which led to the above accepted configuration of the monoximes.

Two molecules of hydroxylamine convert benzil into two isomeric benzil dioximes,

the a- melting at 237° and the β - at 207°. A third y-benzil dioxime has been proposed from y-benzil monoxime; it melts at 163°. The β -dioxime is the most stable; the other modifications rapidly change to it. Under certain conditions the y-dioxime resumes

itself into the α -form (A. 274, 33).

Three different esters are produced with acid anhydrides: bessil-discrime discretis—the α -form melting at 148°, the β - at 124°, and the γ - at 114°. Sodium hydroxide saponifies the α - and β -discretates to their oximes, while the γ -acetate yields the anhy-CHC: N dride, CaHaC: N >0, diphenylfurenane (see this), which also results from all three dioximes by the exit of water. Potassium ferricyanide, in alkaline solution, oxidises all $C_0H_0C=N-O$, melting at 114°. This, when rapidly distilled, three to the person $C_sH_sC=N-$

breaks down into two molecules of phenylcyanate.

A complete picture is also afforded by the deportment of the three dioximes in the Beckmann rearrangement, which has led to a formula for the present case of isomeri on the assumption that the oxime hydroxyls invariably exchange positions with the atomic

groups adjacent to them (A. 274, I):

I. a-Benzildioxime yields chlorides with PCl, by a change in position first of the one and then of the second hydroxyl, which can be converted into the anhydrides: dileszenylazoxime (see this) and diphenylexybiasole (see this), whose hydrates are included in the following diagram for the sake of clearness:

 γ-Benzildioxime in the first stage of the reaction also yields dibenzenylazoxime, but by a second change in position phenylbensoyl urea is produced:

III. β -Dioxime by a double change in position yields oxamilide:

The ready transition of the y-diacetate into furazane is not in harmony with the preceding configuration of the dioximes; this might rather be expected from the adiacetate.

The analogy of the benzil dioximes with the osazones of dioxosuccinic ester is rather remarkable (1, 528). These osazones also occur in three forms, one of which is the stable and the other two unstable, so that the assumption of similar causes for the ison-

erism is not yet excluded (B. 28, 64).

Aniline and benzil heated to 200° yield benzil monanil, C₆H₆CO. C(NC₆H₆)C(H₆ melting at 106°; on adding P₂O₆ the product is benzil dianil, C₆H₆C(NC₆H₆)C(NC₆H₆).

C₆H₅, melting at 142° (B. 25, 2600; 26, R. 700). Benzil, being an o-diketone, is particularly well adapted for the formation of heterocyclic rings. It condenses with ethylene diamine to a dihydropyrasine derivative, with ortho-diamines to quinoxalines, with o-amido-diphenylamine to a stilbaconium base (see this), with ureas and thiureas to urrines and diuretnes, with semicarbazide to oxydiphenyltriasine, etc. Hydriodic acid reduces it to desoxybenzoin, while chromic acid oxidizes it to benzoic acid. On standing with potassium cyanide and alcohol it breaks down into benzoic acid and benzaldehyde. See B. 28, R. 465; 29, R. 645, 865; C., 1897, I, 596, for the condensation of benzil with melonic ester and acetoacetic ester.

The conversion of benzil into benzilic acid (p. 369) by fusion with caustic potash or **epon** boiling with alcoholic potash is important:

$$C_aH_5$$
. CO. CO. $C_aH_5 \xrightarrow{H_2O} (C_8H_5)_2C(OH)COOH$.

Phosphorus pentachloride changes benzil to chlorobenzil, C_aH₅. COCCl₂C₆H₅, melting at 61°, and later to tolane tetrachloride, C_aH₅CCl₂CCl₂C₆H₅, melting at 163°. The latter has also been obtained synthetically on heating benzotrichloride with copper, whereas benzil is produced when it is heated together with glacial acetic acid or sulphuric

As benzil is obtained from benzoin, so anisil, (CH₃O.C₆H₄CO)₂, melting at 133°, cuminil, $(C_3H_7, C_6H_4CO)_3$, melting at 84°, have been prepared by the action of nitric acid upon anisoln and cuminoln (p. 372). Anisil and a hexamethoxybenzil, [(CH₃-O)₃C₆H₄CO]₃, melting at 189°, have been obtained by alkaline reducing agents from anisamide and trimethylgallamide (B. 24, R. 523).

These benzils, when fused with caustic potash, yield:

Anisilic Acid, Cumilic Acid, and Hexamethoxybenzilic Acid (p. 369).

2. Alcohol Derivatives of Stilbene are not known in a free condition; when their esters are saponified, isomeric ketones are obtained for the most part (see phenylvinyl **alcohols**, p. 271):

Bromstilbene $C_gH_gCBr:CH.C_gH_g \xrightarrow{H_gO} \rightarrow C_gH_g.CO.CH_g.C_gH_g$ Desoxybenzoin. **Isobenzil** $C_aH_aC(OCOC_aH_a):C(OCOC_aH_a)C_aH_a \rightarrow C_aH_aCO.CH(OH).C_aH_a$ Benzoin.

However, benzoln reacts in most cases as if it were an unsaturated glycol with the

formula $C_4H_5C(OH):C(OH)C_4H_5$.

Monochlorstilbene, $C_6H_5CH:CCl.C_6H_5$, is an oil, boiling at 320-324°. It is produced when PCl_s acts upon desoxybenzoin, and by the action of alcoholic potash on stil-bene dichloride. When boiled with glacial acetic acid it is transformed into an isomeric modification, melting at 54°. Chlorine and bromine convert it into chloratilbene dichloride, C₆H₅CCl₂. CHCl. C₆H₅, melting at 103°, and chloratilbene dibromide, melting at 127° (C., 1897, 1, 858). Methyl chloratilbene, C₈H₅C(CH₃): CClC₆H₅, is obtained from methyldesoxybenzoln and deports itself similarly. It is an oil, and melts at 118° (B. 25, 2237; 29, R. 34). Monobromstilbene, melting at 31°, results on treating stilbene dibromide, melting at 110°, with alcoholic potash; whereas the stilbene dibromide, melting at 237°, yields a liquid bromstilbene. On the application of heat the oil passes into the solid isomeride; the latter, by further action of caustic potash, changes more readily to tolane than the liquid isomeride. Therefore, this probably has the symconfiguration (B. 28, 2700).

Isobenzil, Stilbene-glycol Dibenzoate, C₆H₅C(O.COC₆H₅): C(OCOC₆H₅)C₆H₆, colorless needles, melting at 156°, is obtained by the action of metallic sodium upon the ethereal solution of benzoyl chloride (compare 1, 297). It is a polymeride of benzil. When saponified with caustic potash it is resolved into benzoic acid and benzoin (B. 24,

1264)

Dichlorstilbene, Tolane Dichloride, C_6H_6CCl : CCl. C_6H_5 , exists in two modifications: a-, melting at 143°, and the β - at 63°. Both are formed by the addition of chlorine to tolane, or by the reduction of tolane tetrachloride with iron and acetic acid, as well as from chlorstilbene dichloride (see above) with caustic potash. Chlorbromstilbene, CaHaCCl: CBrCaHa melting at 174°, is similarly prepared from chlorstilbene dibromide. Dibromstilbenes, a- melting at 208° and β - melting at 64°, are obtained from tolane $C_8H_5C:CC_9H_5$

and bromine. Totallyl Sulphide, Tolane Sulphide, , melting at 174°,

is very probably the anhydride of a thiostilbene glycol. It is formed, together with stilbene,

on heating benzyl sulphide (B. 24, 3313).

3. Carboxylic Acids of the Dibenzyl Group are (a) those in which the carboxyl group is in the benzene nucleus; (b) such as have the carboxyl group in the side-chain: diphenylated fatty acids.

The first group is composed chiefly of a series of o-carboxylic acids produced by phthalic anhydride condensations:

(a) o Desoxybenzoin Carboxylic Acid, CeHa. CHa. CO. CaHa. COOH(+Ha0), melting at 75°, is formed when boiling alkalies act on the corresponding lactone. Ben-

zylidene Phthalide, Benzal Phthalide, CaH4. CH: CCaH4COO, melting at 990, which results from the condensation of phthalic anhydride and phenylacetic acid with the elimination of CO₂.

By means of nitrobenzalphthalide, benzalphthalide can be changed to isobenzal-

phthalide, $C_6H_5C: CH: C_6H_4$. COO), melting at 91°, the anhydride of β ,0 describenzoin carboxylic acid, C_6H_5 . CO. CH₅. C_6H_4 . CO₂H, melting at 163°. The latter is made by decomposing β -phenylhydrindone (p. 387) with caustic soda. Benzalphthal ide sustains a different rearrangement under the influence of sodium alcoholate; the sodium salt of β -phenyldiketohydrindene (p. 388) is then produced:

$$\begin{array}{c} C_{8}H_{5}. \text{ $C: CH: $C_{8}H_{4}: COO$} \leftarrow C_{8}H_{5}CH: \text{$C: C_{8}H_{4}: COO$} \rightarrow C_{8}H_{4}CH: CO: C_{8}H_{4}.COO \\ \text{Isobenzalphthalide} & \text{Benzalphthalide} & \text{Phenyldiketohydriadese.} \end{array}$$

Hydrazine converts benzalphthalide into benzylphthalazone, CgH8.CH3.C.CgH4.CO. By reduction with glacial acetic acid and zinc it passes into benzylphthalimidine, C₆H₅CH₂. CHC₆H₄. CO. NH, melting at 137°. It can also be obtained by the reduc-

tion of benzalphthalimidine (B. 29, 1434, 2743).
0,0 Desoxybenzoin Dicarboxylic Acid, COOH . C₈H₄ . CH₂ . CO . C₈H₄ . COOH, melting at 239°, is obtained upon heating phthalic anhydride with o-carbophenylacetic acid and sodium acetate (B. 24, 2820). The reduction of desoxybenzoin-mono and dicarboxylic acids yields dibenzyl mono- and di- carboxylic acids, melting at 131° and 225° . The oxidation of o-desoxybenzoln carboxylic acid produces o-benzil-carboxylic acid, C_6H_5 . CO. CO. C_6H_4 . COOH, occurring in two modifications, one yellow in color, melting at 141°, and another white, melting at 125-130° (B. 23, 1344, . 2079; **29**, 2745).

0,0 Benzil Dicarboxylic Acid, (COOH. C6H4. CO)2, is white and melts at 270°. It forms two series of dialkyl esters—white and yellow in color respectively. The acid is formed from phthalic anhydride with zinc-dust and acetic acid and subsequent oxida-

tion, or by the oxidation of Diphthalyl, O. OC. C₆H₄C: CC₆H₄COO, melting at 234°. This latter body has been produced by the condensation of phthalide (p. 234) and phthalic anhydride with potassium cyanide (see formation of benzoin, p. 372).

methoxydiphthalyl, $O \cdot OC \cdot C_6H_2(OCH_3)_2C : CC_6H_2(OCH_3)COO$ (B. 24, R. 820; compare B. 26, 540), is similarly made by the condensation of opianic ester. Dihydro-

diphthalyldiimide, NH. CO. C. H., CH. CHC. H. CO. NH, melting with decomposition at 284°, results from the condensation of two molecules of phthalic anhydride with methyl alcoholic ammonia. This substance is isomeric with indigo white (compare B. 29, 2745).

(h) Dibenzyl Carboxylic Acid, a-Phenylhydrocinnamic Acid, a,β-Diphenyl-pio-(b) Didenzyl Cardoxylic Acid, a Thenylayaroximamic Acid, a pp-Diphenyl Prionic Acid, C₆H₅CH₂CH₂CH₂C₆H₅COOH, appears in three physical isomerides, melting at 95°, 89°, 82°, boiling at 335° (B. 25, 2017). Its nitrile results upon introducing benzyl into benzyl cyanide. a-Phenyl-o-amidohydrocinnamic Acid, melting at 148°, is obtained in the reduction of a-phenyl-o-nitrocinnamic acid (B. 28, R. 391). It changes CH₂—CH(C₆H₅)CO very readily into its lactone—β-phenylhydrocarbostyril, C₆H₄

NH

melting at 174°.

Stilbene Carboxylic Acid, a-Phenylcinnamic Acid, CaHaCH: C(CaHa)CO2H, melting at 172°, is formed in the condensation of benzaldehyde with phenylacetic acid. By reduction it becomes a-phenylhydrocinnamic acid, but does not add bromine. The action of bromine upon the sodium salt produces bromstilbene (B. 26, 659). a-Phenylo-amido-cinnamic Acid, melting at 186°, the reduction product of o-nitro-a-phenyl-cinnamic acid, obtained in the condensation of o-nitrobenzaldehyde with phenylacetic acid, yields β -phenanthrene carboxylic acid (see this) (B. 29, 496) when its diazo-derivative is shaken with copper in powder form.

Desylacetic Acid, β -Phenylbenzoyl Propionic Acid, C_6H_5 . COCH(C_6H_5). CH₂.-COOH, melting at 161°, is obtained as ester from the interaction of sodium desoxybenzoin and chloracetic ester. When distilled in vacuum it changes to diphenylcrotolac-

tone, C₆H₅C: C(C₆H₅)CH₂COO, melting at 151° (B. 25, R. 419). See B. 29, 2585, for the formation of desylacetic acid from the condensation product of benzaldehyde with phenylpyroracemic acid.

Dibenzyl-dicarboxylic Acid, sym. Diphenyl-succinic Acid,

CH, CH, COOH

C₂H₄.CH.COOH, occurs similarly to the dialkyl succinic acids in two isomeric forms. The a-acid (+ H₂O) is produced on heating phenyl-bromacetic acid (2 mols.) with alcoholic CNK, also (together with the β -acid, melting at 229°) from stilbene dicarboxylic acid with sodium amalgam. The acid, containing one molecule of water, melts at 185° when rapidly heated; it loses water and remelts at 220°. When heated to 200° with **hydrochloric** acid it changes to the β -acid. Its *anhydride*, melting at 116°, is readily

produced by means of acetyl chloride. The β -acid yields an anhydride (but with more difficulty) when heated with acetyl

chloride (B. 23, 117, R. 574; A. 259, 61). It melts at 112°.

The mitriles, C₆H₆CH(CN)CH(CN)C₆H₆, the a-melting at 160° and the β-melting at 240°, result from the condensation of phenyl-acetonitrile with mandelo-nitrile by means of potassium cyanide (B. 25, 289; 26, 60). Both nitriles yield the β -acid when they are saponified.

Stilbene Dicarboxylic Acid, Diphenyl Maleic Acid, decomposes immediately when separated from its salts, like the dialkylic maleic acids, into water and its anhy-

C₆H₆. C. CO O, melting at 155°. The latter condenses, like phthalic anhydride, С, н, . с . со

dride, with phenylacetic acid and quickly changes to benzaldiphenylmaleid,

 $C_aH_5C-C=CH\cdot C_aH_5$

C₆H₆C = CO >0, which deports itself just like benzalphthalide (p. 376) (B. 24, 3854). The salts of diphenylmaleic acid are formed when dicyanstilbene, C₆H₅C. (CN): C(CN)C₆H₅, melting at 158°, are saponified with alcoholic potash. This nitrile is produced when phenylchloracetonitrile is treated with CNK or NaOC₂H₅, or by the action of sodium alcoholate and iodine upon phenylacetonitrile (B. 25, 285, 1680).

4,5-Diphenyloctan-2,7-dion, C₆H₅. CH. CH₂. CO. CH₃, melting at 161° and boiling at 335-340°, may be regarded as a derivative of dibenzyl. It might be designated a, \(\beta-diacetonyl-dibenzyl. It results in the reduction of 2 molecules of benzylidene acetone in feebly acid or neutral solution (B. 29, 380, 2121).

C. Tri- and Tetra-phenyl Ethane Group.

A triphenyl ethane, (C₂H₅)₂CH. CH₂. C₄H₅, is not known (see C., 1897, 1, 1204).

Triphenyl Ethanon, or *Triphenylvinyl Alcohol*, (C₆H₅)₂. CH. CO. C₆H₅, or (C₆H₅)₂.

C:C(OH)C₆H₅, melting at 136°, results from the action of benzene and aluminium chloride upon chloral, upon dichlor or trichloracetyl chloride (B. 29, R. 292; A. 296, 219). Potassium permanganate oxidizes it to benzophenone and benzoic acid, while alcoholic potash resolves it into diphenylmethane and benzoic acid. Bromine in carbon disulphide converts it into Triphenyl-bromethanon, $(C_6H_6)_2CBrCOC_6H_6$, melting at 97°, in glacial acetic acid, however, by replacement of bromine with hydroxyl triphenyloxyethanon results. It does not react with phenylhydrazine. With hydroxylamine hydrochloride in alcoholic solution, oxidation takes place and triphenylethoxyethanon, (C₈H₅)₂C(OC₂H₅)COC₆H₅, is produced. Caustic potash breaks this body down into benshydrol-ether and benzoic acid.

Triphenylmethyl Ethane, a,a,β-Triphenylpropane, (C₀H₅)₂CH . CH(CH₃)C₆H₆ is probably the product obtained by the reduction of diphenylindone (p. 386) with phosphorus and hydriodic acid. Diphenylindone is an intermediate product in the con-

densation of benzophenone chloride with phenylacetic ester, whereby there results— Triphenyl Acrylic Ester, (C₄H₅)₂C: C(C₄H₅)COOR. The acid, melting at 213°, corresponding to this ester is obtained from its mirrie, melting at 163°, the condensation product of benzophenone chloride and benzyl cyanide (B. 28, 2784; 29, 2841). When

product of benzophenone chloride and benzyl cyanide (B. 28, 2754; 29, 2541). When diphenylindone is fused with caustic potash it yields an acid, melting at 186°, which is isomeric with triphenyl acrylic acid. It is probably—

a.,3. Diphenylvinyl-o-benzoic Acid, COOH[2]C₆H₄C(C₆H₅): CH. C₆H₅. Both acids, when heated with ZnCl₂, revert again to diphenylindone (B. 30, 1282).

Tetraphenyl Ethane, (C₆H₅)₂CH. CH(C₆H₅)₂, melting at 209° and boiling at 379-383°, is formed when benzophenone (p. 345) or benzohydrol chloride, (C₆H₆)₂CHC (p. 344), is heated with zinc, and thiobenzophenone (p. 346) with copper; further, by the reduction of tetraphenylethylene with sodium and alcohol, of benzpinacone or benzinged in a second solice (see below) with hydrodic acid and phosphorus as well as by the condent pinacoline (see below) with hydriodic acid and phosphorus, as well as by the condensation of stilbene bromide, of tetrabromethane, or of chloral with benzene and Al.Cl. (B.

18, 657; 26, 1952; A. 296, 221).

Tetraphenyl Ethylene, $(C_6H_5)_2C:C(C_6H_5)_2$, melting at 221°, is formed, together with tetraphenyl ethane, from benzophenone, and is also obtained on heating benzophenone. none chloride with silver or with zinc-dust, together with the benzpinacolines (B. 29, 1780). Both hydrocarbons are split into two molecules of benzophenone when

The alcohols of the tetraphenyl group are the pinacones of benzophenone and its homologues. They are formed, like the pinacones of the aliphatic series, from the ketones, together with secondary alcohols, by the action of nascent hydrogen.

Benzpinacone, Tetraphenylethylene Glycol, (C₆H₅)₂C(OH)C(OH)(C₆H₅)₂, melts at 185° and splits into benzophenone and benzhydrol. It sustains a like change when boiled with alcoholic potash. It is formed from benzophenone by the action of zinc and sulphuric acid or by the decomposition of sodium benzophenone (B. 25, R. 15).

On heating benzpinacone with hydrochloric or dilute sulphuric acid to 200°, by the action of methyl chloride upon it, or of zinc-dust and acetyl chloride upon benzophenome,

we get two

Benzpinacolines—the a-, melting at 205°; the β - variety, at 179°. So far as their structure is concerned, they are imperfectly known (B. 24, R. 664).

Tetraphenylethane Dicarboxylic Acid, Tetraphenyl Succinic Acid,

(C₆II₂)₂C. COOII melting at 261° with decomposition (its ethyl ester at 89°), is obtained from diphenyl chloracetic ester by the action of silver (B. 22, 1538). Its nitrik, melting at 215°, is formed by the interaction of the nitrile of diphenylacetic acid with sodium

The dilactone of a Benzpinacone-o₂-dicarboxylic Acid, O.CO. C_aH_aC(C_aH_s). C(C₆H₅)C₆H₄COO, melting at 265°, is formed on boiling o-benzoylbenzoic acid (p. 35°)

with hydriodic acid and phosphorus (B. 29, R. 498).

V. ω,ω Diphenylpropane Group: Dibenzylmethane, a,γ-Diphenylpropane, C₆H₅. CH₂. CH₂. CH₃. Cil₁. C₆H₅, boiling at 290-300°, results by the reducing action of hydriodic acid upon Dibenzyl Ketone, C₆H₅. CH₂. CO. CH₂. C₆H₅, melting at 40° and boiling at 330° (B. 24, R. 946). This body is produced in the distillation of calcium phenylacetate. One hydrogen atom of each of the two CH₂ groups can be replaced. by alkyls. It condenses with oxalic ester and sodium ethylate to a Triketo-R-pentence derivative, oxalyldibenzylketone (compare p. 20 and B. 27, 1353; A. 284, 245):

$$CO \left\langle \overset{\text{CII}_2. \ C_6 \text{II}_5}{\text{CII}_2. \ C_6 \text{II}_5} + \overset{\text{COOH}}{\overset{\text{COOH}}{\text{COOH}}} \right\rangle CO \left\langle \overset{\text{CH}(C_6 \text{H}_6) - \text{CO}}{\text{CH}(C_6 \text{H}_6) - \text{CO}} \right\rangle$$

Sodium reduces dibenzylketone to dibenzylcarbinol, $(C_0H_6.CH_2)_2CH.OH$, boiling at 327°. It combines to dibenzyldiphenol methane, $(C_0H_6CH_2)_2C(C_0H_4OH)_2$ (B. 25)

ith phenol. Benzylacetophenone, $C_6H_5CH_2$. CH_2 . CO. C_6H_5 . m. p. 73°, is with dibenzylketone. It is produced on reducing benzylidene acetophenone, : CH. CO. C_6H_5 (m. p. 58°, b. p. 346°), with zinc-dust and acetic acid. This apound is the condensation-product of benzaldehyde and acetophenone (B. 20, combines with hydrochloric acid to chlorbenzylacetophenone:

C1. CH₂. CO. C₆H₅
$$\leftarrow$$
 HCl C₆H₅CH: CH. CO. C₆H₅ $\xrightarrow{\text{H2}}$ C₄H₅CH₂. CH₄. CO. C₆H₆ nzylacetophenone.

, p-Oxybenzylideneacetophenone, from the corresponding oxybenzalded acetophenone, melt at 154° with decomposition, at 160°, and 183°. Alcoholic neverts acetyl-o-oxybenzylideneacetophenone into benzoylcumarone (see this),

H. C. CO. C₆H₆. Reduction changes o-oxybenzylidene acetophenone into l-y-(o-oxyphenyl)propyl alcohol, HO. C₆H₄. CH₂. CH₂. CH(OH)-C₆H₅, at 97°, which is condensed by HCl in methyl alcohol to a-phenylcumaran, H₂. CH₂. (B. 29, 244, 375).

— CH. C₆H₅ (B. 29, 244, 375).

ondensation of 2 mols. of acetophenone by heat alone, or by zinc ethide or zinc yields a homologue of benzalacetophenone, called Dypnone, C_aH_b . $C(CH_3)$: . C_aH_b , melting at 225° (22 mm.), which sustains the same relation to aceto-as mesityl oxide bears to acetone (B. 27, R. 339); see also triphenyl benzene

ldehyde condenses as readily as acetophenone with desoxybenzoln (p. 371), e influence of alkalies, forming benzylidenedesoxybenzoln, $C_6H_5CH:C(C_6-C_6H_5)$, melting at 101°. This also results in the distillation of benzamarone (p. lupon reduction yields benzyldesoxybenzoln, C_6H_5 . CH_2 . $CH(C_6H_8)CO$. C_6 ing at 120°. This can also be prepared by the introduction of the benzyl group into nzoln (see p. 371). If benzaldehyde and desoxybenzoln be condensed through by of hydrochloric acid, there is formed: chlorbenzyldesoxybenzoln, which readily convert into the unsaturated ketone, while by distillation it is resolved and benzoyl chloride (B. 26, 447, 818):

120yl Methane, $(C_6H_5CO)_2CH_2$, is formed from dibenzoyl acetic acid. It 81°. Nitrous acid converts into an isonitroso derivative, $(C_6H_5 \cdot CO)_2C : N$.

ch may be converted into the corresponding envil Triketone, C_6H_5 . CO. CO. CO. C_6H_5 , boiling at 289° (175 mm. prest solidifies to a golden-yellow mass, melting at 70°. It combines with water to

is hydrate (B. 23, 3378).

Exoylacetylmethane, Dibenzoylacetone, occurs in two forms, one of which represents the diketohydroxyl form, $(C_6H_5, CO)_4C: C(OH)CH_3$ (a-, m. p. 80°), the triketo form, $(C_6H_5CO)_2. CH. COCH_3$ (β -, m. p. 107-110°). It results zeoyl acetone and benzoyl chloride with soda. Similarly, dibenzoylmethane, $(C_6H_5CO)_3CH$, melting at 225°. By boiling with and acetic ester this β -modification is changed to the a-form, $(C_6H_5CO)_2C: C-I_6$, soluble in alkalies (A. 291, 25).

rylic Acids: Dibenzyl Acetic Acid, (C₆H₅, CH₂)₂CH. COOH, melting at rived from dibenzyl malonic acid, (C₆H₅CH₂)₂C(COOH)₂, the ester of which ed by benzylating malonic ester. 0,0-Dinitrobenzyl Acetic Acid,

H₂—CH—CH₂
C₆H₄, made in an analogous manner, may be condensed tion with zinc-dust to tetrahydronaphtinolin (see this) (B. 27, 2248; 29, 636).

**ryl Malonitrile, (C₆H₆CH₃)C(CN)₂, melting at 130° and boiling at 360° is from the corresponding nitrilo-acid amide, which is prepared from

amide. Sodium and alcohol reduce the nitrile with elimination of a cyanogen group to dibenzylethylamine, (CaHaCH2)3CH. CH2. NH2, whose hydrochloride melts at 190°

(B. 29, R. 1111).

Dibenzyl Glycollic Acid, (C₆H₅. CH₂)₂C(OH). CO₂H, Oxatolylic Acid, is produced from dibenzyl ketone by means of CNK and hydrochloric acid, and when value and pulvic acids are boiled with dilute alkalies. It melts at 156°. When boiled with concentrated potassium hydroxide it decomposes into oxalic acid and two molecules of toluene (A. 219, 41).

a Phenyl & benzoylpropionic Acid, Phenylphenacyl Acetic Acid, CaH, CO. CH, .. cH₁C₈H₅C(X)H, melts at 153°. Its *mitrile* melts at 127°. The acid is produced when cNK acts upon chlorbenzylacetophenone (p. 379). If heated with acetic anhydride it yields

the lactone of isomeric a, Diphenyl-)-oxycrotonic Acid, CaH, C: CH.CH(CaH,)COO, melting at 110°, while upon reduction with sodium amalgam, a,) Diphenylbutyro-

lactone, C₈H₅. CH. CH₂. CH(C₆H₅)COO (A. 284, 1).

a₁)-Diphenylacetoacetic Acid is isomeric with phenylphenacylacetic acid. Its etter, C₆H₅. CH₂. CO. CH(C₆H₅)CO₂C₂H₅, melting at 79°, is formed when two molecules of phenylacetic ester are condensed with sodium ethylate. Concentrated sulphuric acid

condenses the ester to a naphthalene derivative—phenylnaphthoresorcinol (A. 296, I).

Dibenzoyl Acetic Acid, (C₆H₅, CO)₂CH, COOH, melts at 109°. Its ester, from benzoyl acetic ester and benzoyl chloride, yields CO₂ and dibenzyl methane by dry distillation, and acetophenone, carbon dioxide, and benzoic acid when digested with sulphuric acid.

VI. ...-DIPHENYL BUTANE GROUP.

Dibenzyl Ethane, a,d Diphenylbutane, C6H5. CH2. CH2. CH2. CH3. CH3. melting at 52°, is formed by the reduction of Diphenylbutylene, C.H. CH. (112. C112. C6113, which is produced when sodium and alcohol act upon the nitrile of a phenyleinnamenyl acrylic acid (B. 23, 2857). Diphenyldiethylene, CaH3. CH: CII. CII: CII. C₆II₅, melting at 148° and boiling at 250°, results on heating a-phenyl-cinnamenyl acrylic acid (B. 23, R. 333). A tetra-iodide of this hydrocarbon, C₆H₆Cl:-CI. CI: CIC₆II₅, melting at 144° (B. 26, R. 19), is formed by the addition of iodine to

Diphenyl Diacetylene, C₆H₅C : C.C : C.C₆H₆, melting at 88°. This is made by shaking copper phenyl acetylide, C₆H₅C : C. Cu (p. 268), in ammoniacal solution with air, or by the action of potassium ferricyanide. It is the parent hydrocarbon of indigo blue. Its 0,0-dinitro-derivative, $C_6H_4 < \begin{array}{ccc} C & C & C \\ O_2N \end{array} > C_6H_4$ (from 0-nitro-phenyl acetylene, p. 268), is rearranged by concentrated sulphuric acid into the isomeric di-isatogen (see this), which becomes indigo blue: $C_6H_4 < \frac{CO}{NH} > C: C < \frac{CO}{NH} > C_6H_4$ by reduction with ammonium sulphide (B. 15, 53).

Ketones: Phenethyl Benzyl Ketone, CeH5. CH2. CH2. CO. CH2. CeH5, boiling at 324° to 336°, is produced when hydrocornicularic acid is distilled with lime (p. 382). Diphenacyl, Dibenzoyl Ethane, Callo CO. CH2. CH2. CO. Callo, melting at 145°, is made from phenacyl benzoylacetic ester (p. 371), as well as by the reduction of the two bromdiphenacylens, melting at 129° and 161°, with magnesium powder. These bromides are produced when sodium ethylate acts upon phenacyl bromide (B. 29, 1750, Being a y diketone, it readily forms diphenylfurfurane, diphenylthiophene, and diphenylpyrrol.

Desylacetophenone, a,β-Dibenzoyl Phenyl Ethane, C₆H₅CO . CH(C₆H₅) . CH₁ COC 6116, melting at 126°, is produced in the condensation of benzoin and acetophenone with potassium cyanide (B. 23, R. 636; 26, 60). See B. 29, R. 171, for the action of

Bidesyl, C₆H₅. COCH. C₆H₅, dibenzoyl-dibenzyl, results when desylbromide or C₆H₅. CO. CH. C₆H₅. iodine acts upon sodium desoxybenzoln (B. 21, 1355; 25, 285). It melts at 255°. Iso-bidesyl, formed simultaneously, melts at 161°. Bidesyl yields tetraphenyl pyrrol and tetraphenyl furfurane, the so-called lepidene.

a,β-Dibenzoyl Styrene, Anhydroacetophenone Benzil, C₆H₆CO.-CH: C(C₆H₆)COC₆H₆, melting at 129°, is obtained from benzil and acetophenone by the action of caustic potash. When heated it rearranges itself by the migration of a phenyl group into the isomeric triphenylcrotolactone, melting at 118°:

$$CO \longrightarrow C$$
 $C_6H_5CO \cdot C(C_6H_5) : CHCOC_6H_5 \longrightarrow (C_6H_5)_2 \stackrel{\cdot}{C} \cdot CH : \stackrel{\cdot}{C}C_6H_5$
Dibenzoyl Styrene
 a,a,γ -Triphenylcrotolactone.

Dibenzoyl Stilbene, acicular oxylepidene, C₆H₅CO.C(C₆H₆): C-(C₆H₆)COC₆H₅, melting at 220°, resulting from the oxidation of lepidene (see above) with nitric acid, or of thionessal (p. 370) with potassium chlorate and hydrochloric acid, also yields, on heating, tetraphenylcrotolactone, tabular oxylepidene, melting at 136°:

$$\begin{array}{c} \text{CO} \longrightarrow \text{O} \\ \text{C}_{\mathbf{g}} \text{H}_{\mathbf{g}} \text{COC}(\text{C}_{\mathbf{g}} \text{H}_{\mathbf{g}}) : \text{C}(\text{C}_{\mathbf{g}} \text{H}_{\mathbf{g}}) \text{COC}_{\mathbf{g}} \text{H}_{\mathbf{g}} \longrightarrow \\ \text{Dibenzoyl Stilbene} \\ \text{C}_{\mathbf{g}} \text{H}_{\mathbf{g}} \text{COC}(\text{C}_{\mathbf{g}} \text{H}_{\mathbf{g}}) : \overset{\bullet}{\text{C}}(\text{C}_{\mathbf{g}} \text{H}_{\mathbf{g}}) : \overset{\bullet}{\text{C}}(\text{C}_{\mathbf{g}} \text{H}_{\mathbf{g}}) \\ \text{a.e.}, \beta, \gamma \text{-} \text{Tetraphenyl crotolactone.} \end{array}$$

Consult B. 24, 510; 25, R. 418, for the action of phenylhydrazine upon dibenzoyl styrene and stilbene. Bidesyl results from the reduction of dibenzoyl-stilbene.

Diphenyltetraketone, C₆H₅. CO. CO. CO. CO. C₆H₅(+H₂O), melting at 87°, is red in color when hydrous, and yellow when anhydrous. It is formed in the oxidation of Benzoyl Formoin, C₆H₅. CO. CO. CH(OII)COC₆H₅, melting at 170°, which is produced like benzoln from benzaldehyde by condensing two molecules of phenyl glyoxal with potassium cyanide. Benzoyl formoin also results readily from the action of soda upon isonitroso-acetophenone acetate, CaH5. CO. CH: NO. COCII3. Substituted diphenyltetraketones have been similarly prepared (B. 25, 3468).

Diphenyltetraketone is a member of the following homologous series:

Diphenyl Diketone, Benzil,
$$C_6H_5$$
CO. COC_6H_5 (p. 373). Diphenyl Triketone, C_6H_5 . CO. CO. CO. C_6H_5 (p. 379). Diphenyl Tetraketone, C_6H_5 . CO. CO. CO. CO. C_6H_5 .

Hydroxylamine forms but one 1,4-dioxime [C₆H₅C(NOH)CO]₂, melting at 176° with decomposition; the 2,3-dioxime or dibensoylglyoxime, C₆H₅. COC(NOH)C(NOH)CO-Calls, melting with decomposition at 108°, results from the reduction of its peroxide, which is formed in the interaction of nitric acid and acetophenone. Hydroxylamine converts the 2,3-dioxime into diphenyltetraketoxime, CeH5[C(NOII)]4CeH5, melting at 225° (B. 26, 528).

Carboxylic Acids: a-Phenylcinnamenyl Acrylic Acid, C₆H₅CH: CH: CH: CC(C₆H₅)COOH, melting at 188°, and its dioxymethylene derivative, a-Phenyl Piperic Acid, melting at 209°, are obtained from cinnamic aldehyde and piperonyl acrolein with

phenylacetic acid by means of Perkin's reaction (B. 28, 1189).

The ester of benzoyl phenacyl-acetic acid, a,β-dibencoyl propionic acid, C₆H₈.

CO. CH₂. CH(CO. C₆H₈)COOR, is obtained from benzoyl acetic ester with phenacyl bromide (p. 249). In the ketone decomposition it yields diphenacyl (p. 380). the acid decomposition, benzoyl propionic acid (p. 260) and benzoic acid.

dibenzylketone, melting at 240–242°, may be referred to benzoyloxalylphenylacetic acid, C_6H_5 . CH_2 . CO . CO . CH(C_8H_6). COOH, isomeric with dibenzoylpropionic acid. It is formed on heating oxalyldibenzylketone (p. 378) beyond its melting point (A. 284, 293):

$$C_{\mathbf{e}}H_{\mathbf{s}}C:C(OH).CO.CH.C_{\mathbf{e}}H_{\mathbf{s}}\longrightarrow C_{\mathbf{e}}H_{\mathbf{e}}C:C(OH).C:CH.C_{\mathbf{e}}H_{\mathbf{s}}$$

Alkalies convert isoxalylbenzylketone, just like pulvic acid richer in CO2, into dibenzyl

glycollic acid.

Dibenzylidene Succinic Acid, C₆II₈CH:C(COOH). C(COOH): CHC₆H₅, melting with decomposition at 201°, and benzylidene-y-diphenylitaconic acid, (C₆H₅)₁C:U(COH). C(COOH): CH. C₆H₅, are obtained by the condensation of succinic ester (1) with two molecules of benzaldehyde, and (2) with benzophenone and benzaldehyde by means of sodium ethylate (B. 30, 94).

Dibenzoyl Succinic Acid

C₆H₅. CO. CH. CO₂H

Dibenzoyl Succinic Acid, C_6H_5 . CO. CH. CO₂H.

Its ethyl ester, melting at 129°, is obtained from sodium benzoyl acetic ester by the action of iodine, just as we form diaceto-succinic ester from acetoacetic ester. By the elimination of water there results diphenyl-furfurane dicarboxylic ester. The esters of the acid appear in three forms, of which the unstable (labile) variety, soluble in alkalies, is probably the enol-form, [C₄H₅·C(OH): C(COOH-]₂, while the other two represent the syn- and anti-modifications of the keto-form (B. 29, R. 962).

Diphenyloxalyl Diacetic Acid, Diphenylketipic Acid, COOH . CH(C₆H₅)CO . CO. CH(C₆H₅)COOH, is isomeric with dibenzoylsuccinic acid. Its dimitrile, melting at 270° with decomposition, is produced by the condensation of oxalic ester with two molecules of benzyl cyanide. When saponified with hydrochloric or sulphuric acid it yields not the free acid, but passes at once into its anhydride, a monolactone, Pulvic Acid,

OOC. CH(C₆H₅)CO. C: C(C₆H₅)COOH, melting at 214°, and a dilactone,

OOC. $C(C_6H_5): C. C: C(C_6H_5)COO$. Pulvic acid may also be prepared from Vulpic

Acid, $C_{19}II_{14}O_{5}$, consisting of yellow prisms, melting at 110°, and found in a certain moss and in the lichen *Cetraria vulpina*, by boiling it with lime-water. Sodium ethylate converts pulvic acid back into salts of vulpic acid. The latter is therefore very probably to be regarded as a methyl ether of pulvic acid (B. 27, R. 869; A. 288, 14). Zincdust and ammonia reduce pulvic acid to **Hydrocornicularic Acid**, a, b-Diphenyl-lavalinic Acid, C₆II₅. CII₂. CO. CH₂. CH(C₆II₅)COOH, melting at 134°. Distilled with lime, it yields phenylethylbenzyl ketone (p. 380), and when heated with caustic potash the products are toluene and phenylsuccinic acid (p. 262). Boiling alkalies decompose pulvic and vulpic acids into 2CO₂ and dibenzylglycollic acid. If it be assumed that diphenylketipic acid is formed at first, then this reaction, discarding the evolution of CO₂, is an analogue of the benzilic acid transposition (p. 374):

$$\begin{array}{c|c} C_6H_5 \cdot CH(COOH) \cdot CO & + H_2O \\ \hline C_6H_5 \cdot CH(COOH) \cdot CO & -2CO_8 \\ \hline \end{array} \\ \begin{array}{c} C_6H_6 \cdot CH_2 \\ \hline \end{array} \\ \begin{array}{c} C_6H_6 \cdot CH_2 \\ \hline \end{array} \\ \begin{array}{c} C(OH)COOH. \end{array}$$

Ethane-dibenzoyl-0₂-dicarboxylic Acid, COOH. C₆H₄CO. CH₂. CH₃. CO.-C₆H₄. COOH, is another isomeride of dibenzoylsuccinic acid. It melts at 166°. It is made by boiling ethine diphthalyl, O.OC. C₆H₄. C:CH. CH:C. C₆H₄. COO, melting above 350°, the *dilactone* corresponding to it, with alkalies. Ethine diphthalyl results from the condensation of two molecules of phthalic anhydride with succinic acid when two molecules of carbon dioxide are split off (B. 17, 2770). Sodium alcoholate rearranges it into bisdiketohydrindene (p. 388).

VII. ...DIPHENYLPENTANE GROUP.

The hydrocarbons of this group are not known.

Ketones: Dibenzylidene Acetone, CaHBCH: CH. CO. CH: CH. CaHB, yellow needles, melting at II2°, is formed when acctone and benzaldehyde are treated with sodium hydroxide. In the first step benzal acctone is produced (p. 272):

 $CH_1.CO.CH_2$ $\xrightarrow{C_4H_6CHO}$ $\rightarrow C_4H_6CH:CH.CO.CH_2$ $\xrightarrow{C_4H_6CHO}$ $\rightarrow C_4H_6CH:CH.CO.CH:CH.C_6H_6.$

Di-o-cumarketone, (OHC₆H₄CH: CH)₂CO, melting at 160°, is produced in the form of its diglycose compound by the condensation of helicine (see this) with acetone. Cinnamylidene Acetophenone, C₆H₅CH: CH: CH: CH: COC₆H₅, from cinnamic aldehyde and acetophenone, melts at 103°; its oxime, melting at 131°, is condensed to aa₁-diphenylpyridine upon the application of heat (B. 28, 1730).

1,5-Diketones of this group are obtained by condensing benzaldehydes (I mol.) and acetophenones (2 mols.) with sodium hydroxide: benzylidene diacetophenone, C₂H₅CH(CH₂. CO. C₆H₅), melting at 85°, and o-oxybenzylidene diacetophenone, (OH)[2]C₆H₄(CH₂. CO. C₆H₅), melting at 131°. By varying the conditions and condensing two molecules of benzaldehyde with three molecules of acetophenone, two isomeric dibenzylidene-triacetophenones, $(C_6H_5CH)_2(CH_2COC_6H_5)_3$, melting at 198°

and 256° respectively, are produced.

Benzamarone, Benzylidenebisdesoxybenzoin, C₆H₅COCH(C₆H₅)CII(C₆H₅). CII(C₆-H₅)COC₆H₆(?), exists in two modifications, melting at 219° and 180°. It is prepared by condensing benzaldehyde with desoxybenzoin, as well as by the addition of desoxybenzoln to benzylidenedesoxybenzoln (p. 379) by the aid of sodium ethylate. Similarly, desoxybenzoln attaches itself to the unsaturated unions of other olefine derivativese. g., a-phenylcinnamo-nitrile, benzalacetoacetic ester, benzalbenzoylpyroracemic ester, etc. (B. 25, 1087). By decomposition with sodium ethylate benzamarone yields the sodium salt of amaric acid, C₂₃H₂₀O₃, and with sodium isobutylate it forms dimethylamaric acid, C₂₅H₂₀O₃ (A. 275, 50).

The dry distillation of benzamarone produces desoxybenzoin, benzylidene desoxy

zoin, and a body isomeric with the latter (B. 26, 818). Hydroxylamine changes it quite

readily into pentaphenylpyridine.

Carboxyl derivatives of the ω,ω -diphenylpentane group: Diphenacyl Acetic Acid, (C₂H₂COCH₂)₂CH. CO₂H, melting at 133°, is obtained from diphenacyl malonic ester, (C₄H₅COCH₂)₂C(CO₂R)₂, or diphenacyl acetoacetic ester, (C₆H₅COCH₂)₂C(COCH₃)COCC₄H₅, melting at 83°, the reaction-products from phenacyl bromide upon malonic ester and acetoacetic ester (B. 22, 3225). Diphenacyl acetic acid, being an e-diketone, forms a pyridine-derivative with ammonia (B. 29, 798).

VIII. ... DIPHENYL HEXANE GROUP AND HIGHER HOMOLOGUES.

Oxalyldiacetophenone, CaHaCOCH2COCCH2COC6H5, melting at 180°, is formed in the condensation of two molecules of acetophenone and oxalic ester with sodium alcoholate. Consult B. 28, 1206, for the reduction-products of this tetraketone.

ω, ω-Diphenyl Diketohexane, (C₆H₆COCH₂CH₂)₂. Diphenyl Diketo-octane, H₆COCH₂CH₂CH₂, and Diphenyl Diketononane, (C₆H₆CO. CH₂. CH₂. CH₃.)₂. CH₂, are prepared from the chlorides of adipic acid, sebacic acid, and azelaic acid by means of benzene and aluminium chloride (B. 29, R. 1157). Cinnamylene benzylidene acetone, C₂H₅CH: CH: CH: CH: COCH: CHC₆H₅, melting at 106°, is derived from a, a-diphenylheptane. It is formed from cinnamylene acetone and benzaldehyde (B. 20, 615).

B. CONDENSED NUCLEI.

The condensed nuclei to be discussed in the following section are characterized by the fact that in them C-atoms of benzene nuclei participate in the formation of other carbocyclic rings—e. g.:

Although these condensed nuclei, as a rule, continue to manifest their aromatic character, they do, in harmony with their peculiar structure, exhibit in their behavior a series of wide differences from the true benzene compounds (see naphthalene). They are eventually, by suitable oxidations, changed like the homologues of benzene into benzene carboxylic acids. The parent hydrocarbons of these groups occur, like benzene, chiefly in coal-tar, from which they are obtained in greater or lesser amount. Naphthalene is technically important; this is especially true of anthracene, the hydrocarbon of alizarin.

The carbocyclic derivatives of the tri-, tetra-, and pentamethylene series constitute the transition from the fatty bodies with open chain to the benzene derivatives. Similarly, the indene and the hydrindene compounds form the transition members from the fatty aromatic substances with open side-chains to those which contain several condensed benzene nuclei. They represent the coalescence of a benzene nucleus with the five-membered pentene. Very probably pseudophenyl acetic acid (p. 196) contains a united benzene and trimethylene ring.

1. INDENE AND HYDRINDENE GROUP.

Indene has received its name from indol, because of its similarity to the latter in structure. By introducing NH for the methylene group of indene the formula of indol results.

Indene, C₉II₆, is an oil, boiling at 178°; its specific gravity equals 1.040 at 15°. It occurs, together with commarone, to which it is very similar in its behavior (B. 28, 114), in that fraction of coal-tar boiling at 176-182°, and can be extracted from it by means of its

pieric acid derivative (B. 23, 3276). Very appreciable amounts of indene are also present in the condensation products resulting from the chilling of illuminating gas (B. 28, 1331). It can also be obtained by the distillation of the calcium salt of synthetic hydrindene carboxylic acid (p. 387) (B. 27, R. 465). Sulphuric acid resinifies indene. Chlorine and bromine unite with it to dibrom- and dichlorhydrindenes. Like the terpenes (p. 309), it also combines with NOCl and N_2O_3 , forming indene nitrosites, the e-variety melting with decomposition at 108°, and the β -form at 137° (B. 28, 1331). Metallic sodium and alcohol reduce indene to hydrindenes where the absyrgance (as this) molecules of indene unite, with the exit of four hydrogen atoms, to chrysene (see this).

Bz.-Brom-indene, C₂H₂Br(C₂H₄), boiling at 243°, is formed from hydrindene and bromine (B. 26, 2251). It yields bromphthalic acid upon oxidation.

Indene derivatives are obtained synthetically by the following methods, which to some

extent recall the syntheses of the pentamethylene compounds:

(1) Benzene compounds, having the group C_0H_0 . C. C. CO, split off water and condense to indene derivatives: (a) Nitro-a-alkyl cinnamic aldehydes yield amido- β -alkyl indenes (B. 22, 1830):

Similarly, benzyl acetone and benzyl acetoacetic ester yield γ -methylindene and γ -methylindene- β -carboxylic acid (B. 20, 1574; A. 247, 157) when they are heated with sulphuric acid:

$$\begin{array}{c} \text{OC} & \text{-CH}_3\\ \text{C}_6\text{H}_5 & \text{CH}_2 \\ \text{Benzyl Acetone} \end{array} \longrightarrow \begin{array}{c} \text{C}_6\text{H}_4 & \text{CH}_3 \\ \text{CH}_3 & \text{CH}_5 \\ \text{CH}_3 & \text{CH}_4 \\ \text{CH}_5 & \text{CH}_2 \\ \text{CH}_5 & \text{CH}_2 \\ \text{CH}_6 & \text{CO}_2\text{H} \\ \text{Benzylacetoacetic Acid} \end{array} \longrightarrow \begin{array}{c} \text{C}_6\text{H}_4 & \text{CH}_2 \\ \text{CH}_2 & \text{C}_3 & \text{CO}_2\text{H} \\ \text{CH}_2 & \text{C}_3 & \text{CO}_2\text{H} \\ \text{Benzylacetoacetic Acid} \end{array}$$

(b) Substituted cinnamic acids yield indone derivatives when they are treated with hot sulphuric acid, just as the hydrocinnamic acids, alkylized in the nucleus and in the side-chain, yield dihydroindones. Cinnamic and hydrocinnamic acids themselves react with as little readiness as cinnamic aldehyde (A. 247, 140; B. 25, 2095, 2129):

(2) The hydrindene derivatives have been obtained in the same manner as the tetraand pentamethylene derivatives (p. 21): by the action of xylylene halides upon malonic ester and sodium alcoholate (B. 17, 125; 18, 378):

$${\rm C_6H_4}{<}{\rm CH_2^Br}_{Br} + {\rm CNa_2}{<}{\rm CO_2^RR}_{R} = {\rm C_6H_4}{<}{\rm CH_2^*}{>}{\rm C<}{\rm CO_2^RR}_{CO_2^*R}$$

(3 a) The formation of αγ-diketohydrindenes from o-phthalic esters and fatty acid esters or ketones (A. 252, 72; B. 27, 104, R. 19) corresponds to the condensation of oxalic esters to pentamethylene derivatives:

$$C_8H_4 < \stackrel{COOR}{COOR} + H_9C \cdot CO_9R \longrightarrow C_8H_4 < \stackrel{CO}{CO} > CH \cdot CO_8R$$
.

11—33

(3 b) The phthalide compounds (pp. 240, 290) of the formula C_0H_0 CC=CHR $C_0>0$, formed from phthalic anhydride and fatty acids, are transposed by sodium alcoholates into the sodium derivatives of the isomeric diketohydrindenes (B. 26, 954, 2576):

$$C_{e}H_{e} \stackrel{C \longrightarrow CHBr}{\longleftrightarrow} CHBr \longrightarrow C_{e}H_{e} \stackrel{CO}{\longleftrightarrow} CHR.$$

(4) The formation of dihydroindones by the distillation of salts of o-phenylese diacetic acid and o-hydrocinnamic acid (B. 26, 222, R. 708) corresponds to the cyclic ketone formation of dicarboxylic acids of the adipic acid series (p. 21):

$$C_{\mathfrak{g}}H_{\mathfrak{q}} < \overset{CH_{\mathfrak{g}}}{\subset} \overset{COOH}{\longrightarrow} C_{\mathfrak{g}}H_{\mathfrak{q}} < \overset{CH_{\mathfrak{g}}}{\subset} \times COH_{\mathfrak{g}} > CH_{\mathfrak{g}}$$

$$C_{\mathfrak{g}}H_{\mathfrak{q}} < \overset{CH_{\mathfrak{g}}}{\subset} \times CH_{\mathfrak{g}} - CH_{\mathfrak{g}} \times CH_{\mathfrak{g}} + CH_{\mathfrak{g}} \times CH_{\mathfrak{g}} \times CH_{\mathfrak{g}} + CH_{\mathfrak{g}} \times CH_$$

(5) The formation of indene derivatives from naphthalene derivatives is rather remarkable; a six-membered benzene-ring is rearranged to a ring of five members-similar to the production of pentamethylene derivatives from the benzenes, or floorese compounds from phenanthraquinone. This change occurs by the action of chlorine or hypochlorous acid upon the naphthols, naphthoquinones, amidonaphthols, etc. The first product consists of naphthalene keto-derivatives with the groups—CO.CO—or CO.CCl₂—; these sustain the decomposition (B. 20, 2890; 21, 2719). Thus, dichlor-3-naphthoquinone yields dichloroxyindene carboxylic acid:

$$C_6H_4$$
 $CO - CO$
 C_6H_4
 $CC1 = CC1$

Dichlor-\$-naphthoquinone

 C_6H_4
 $CC1 = CC1$

Dichloroxyindene-carboxylic Acid.

Indene Derivatives:)-Methyl Indene, C₈H₄: C₃H₃. CH₈, boiling at 206°, is obtained synthetically from benzyl acetone, and by the elimination of CO₂ from its carboxylic acid. Bz.-Amido-β-methyl-, ethyl-, isopropyl indenes melt at 98°, 89°, and &4° (see above) respectively.

β-Indene Carboxylic Acid, C₆H₄: C₃H₃. CO₂H, melting at 222-230°, is produced by the action of bromine at 100° upon a chloroform solution of hydrindene carboxylic acid (see below).

y-Methyl-3-indene Carboxylic Acid, melting at 200°, is obtained from benzylacetoacetic ester.

 β , Dichlor-a-oxyindene Carboxylic Acid, melting at 100°, is obtained from β -dichlornaphthoquinone. Chromic acid oxidizes it to dichlorindone. It is changed to chlorindone carboxylic acid when digested with concentrated sulphuric acid (B. 28, R. 279).

 a_{ij} 3-Diphenylindone, $C_6 II_4 \stackrel{C(C_6 II_5)}{CO} C(C_6 H_5)$, garnet-red crystals, melting at

151°, is produced, together with triphenylacrylic acid (p. 378), when benzophenone chloride is condensed with phenylacetic ester. It yields triphenyl propane upon reduction. It is decomposed into a,β -diphenylvinyl-o-benzoic acid when fused with caustic potash. It can be recovered from this as well as from triphenylacrylic acid on heating with since chloride (B. 30, 1281).

 $\beta_1\gamma$ -Dichlor- and Dibromindone, C_0H_4 : C_2Br_2O , melting at 90° and 123°, have been obtained synthetically from dichlor- and dibromcinnamic acids. The γ -chlorine atom in these compounds is readily replaced by OH or NHR on digesting them with caustic sods, or fatty or aromatic amines. β -Chlor- and β -Brom- γ -oxyindone melt at 114° and 119°. β -Chlor- and Bromanilido-indone melt at 204° and 170°.

Perchlorindone, CaCla: CaClaO, melting at 149°, is produced by a peculiar reaction

from a pentene-derivative, hexachloroxy-R-pentene carboxylic acid, the decomposition product of hexachlordiketo-R-hexene, on digesting it with water or with a solution of sodium acetate (A. 272, 243; B. 28, 521):

$$\begin{array}{c} \textbf{CCl} = \textbf{CCl} \\ \textbf{2} \\ \textbf{CCl}_2 - \textbf{CCl}_2 \\ \textbf{Exachloroxylentene} \\ \textbf{Carboxylic Acid} \\ \end{array} \\ + \textbf{H}_2\textbf{O} = \begin{array}{c} \textbf{CCl} = \textbf{CCl} - \textbf{C} - \textbf{CCl} \\ \textbf{CCl} = \textbf{CCl} - \textbf{C} - \textbf{CO} \\ \textbf{CCl} = \textbf{CCl} - \textbf{C} - \textbf{CO} \\ \textbf{Perchlorindone.} \\ \end{array} \\ \begin{array}{c} \textbf{CCl} + 3\textbf{CO}_2 + 6\textbf{HCl} \\ \textbf{Perchlorindone.} \\ \end{array}$$

Hydrindene Derivatives: Hydrindene, C₆H₄: C₃H₈, is an oil, boiling at 177°.

results when indene is reduced with sodium and alcohol.

Dichlorhydrindene is an oil. Dibromhydrindene, Calla: Calla Br., melts at 44°. They yield chlor- and bromoxyhydrindenes, melting at 129° and 131°, when digested with water. Ammonia converts the latter bodies, in the cold, into amido-oxyhydrindene, melting at 133°, which nitrous acid transposes into β, γ-dioxyhydrindene, hydrindene glycol, C₆H₄: C₂H₄(OH)₂, melting at 120° (B. 26, 1539).

Hydrindene-β-methyl-, ethyl-, and phenylketones are formed in the distillation

of hydrindene carboxylic acid with benzoic acid, propionic acid, and acetic acid (B. 26,

2351).

Hydrindene- β -carboxylic Acid, $C_4H_4(CH_2)_2CH$. CO_2H , melting at 130°, is converted by distillation of its salts into indene, by bromine into indene-carboxylic acid, and is oxidized by KMnO₄ to o-carbophenylglyoxylic acid (p. 265). It results when CO₂ is eliminated from hydrindene- β -dicarboxylic acid, melting at 199°. The ester of the latter acid may be obtained synthetically from xylylene bromide and malonic ester.

β-Acethydrindene Carboxylic Ester, C₈H₄(CH₂)₃C<COCH₂, is obtained from xylylene bromide and acetoacetic ester.

a-Hydrindone, C₆H₄<CO²>CH₂, melting at 41° and boiling at 244°, is obtained in the dry distillation of o-carbohydrocinnamic acid (p. 245) as well as from o-cyanhydrorinnamic ester (p. 245) upon digesting with concentrated hydrochloric acid. The phenyl-hydrazone melts at 131°. The oxime, melting at 146°, is changed by reduction to a-amidohydrindene, melting at 220°, which N₂O₃ converts into a-oxyhydrindene, melting at 54° (B. 26, R. 708). Phosphorus pentachloride converts a-hydrindonoxime into hydrocarbostyril (Beckmann's transposition) (B. 27, R. 598):

$$C_{e}H_{4} \stackrel{CH_{2}}{\longleftarrow} CH_{2} \xrightarrow{\qquad} C_{e}H_{4} \stackrel{CH_{2}}{\longleftarrow} CH_{2}$$

Hydrindone Azine, C, H,: N.N:C, H,, melting at 165°, results from the action of hydrazine upon the oxime. Nitrous acid converts hydrindone into isonitrosohydrindone, $C_8H_4 < {CH_2 \choose CO} > C = NOH$, melting with decomposition at 210°. This phenylhydrazine changes to an osazone, melting at 229°. The latter is isomeric with the dihydrazone obtained from a, γ -diketohydrindene. It yields β -amido-a-hydrindone when it is reduced (B. 29, 2605, R. 869; C., 1897, I, 860).

When o-, m-, and p-methylhydrocinnamic acids are heated they yield o-, m-, and p-Methyl-a-hydrindones. The constitution of the latter is deduced from their oxidation to the various methyl-o-phthalic acids. Bz.-Chlor-, brom-, iod-, and nitrohydrin-

dones behave similarly (B. 25, 2095).

 β -Methyl-a-hydrindone, melting at 168° (II mm.), and β -Phenyl-a-hydrindone, melting at 78° , are obtained from a-methyl and phenylhydrocinnamic acids. When its ethereal solution is shaken with caustic soda β -phenylhydrindone is changed partly to β -phenyloxyhydrindone, melting at 129°, and in part by rupture of the ring into desoxyhenzoin-o-carboxylic acid, $C_0H_4(CO.OH).CH_2.COC_0H_6$ (p. 376) (B. 26, 2095). γ -Phenyl-a-hydrindone, melting at 78°, is prepared from β , β -diphenyl-propionic acid (B. **26**, 2128).

Tetrachlor-a-hydrindone, CaH4: CaCl4O, melting at 108°, is the addition product of

chlorine and dichlorindone (p. 387). It is readily decomposed by digestion with alcoholic sodium hydrate into o-trichlorvinylbenzoic acid (p. 273). Chlordibrom-hydrindone-) carboxylic Acid, C_8H_4 : $[C_8ClBr_2O(COOH)]$, melting at 171°, is made from chlorindone-) carboxylic acid (p. 387) and bromine. It is similarly decomposed into bromchlormethylene-homophthalic acid (p. 393).

3. Hydrindone, $C_8H_4(CH_2)_2CO$, melting at 61° and boiling with decomposition at

220-225°, is obtained from calcium o-phenylene diacetate (p. 245). Its hydrasone melts at 120°. Its oxime, melting at 155°, yields β-amidohydrindene upon reduction (B. 26,

a.) Diketohydrindene, C₆H₄(CO)₂CH₂, melting with decomposition at 130°, is obtained from its carboxylic acid (below). It consists of colorless needles, which dissolve readily with a yellow color in alkalies. The hydrogen atoms of the methylene groups placed between the two keto-groups have an acid nature. Phenylhydrazine converts it into a monohydrazone, melting at 163°, and a dihydrazone, C.H.(C: NNI-C. 6115)2CH2, melting at 171°. Diazobenzene chloride converts the monohydrazone into a triketohydrindene, $C_gH_g(CO)_2C$: NNHC $_gH_g$, which is also prepared by the decomposition of benzaldiketohydrindene, $C_gH_g(CO)_2C$ = CHC $_gH_g$, a condensation product of benzaldehyde and diketohydrindene, with phenylhydrazine.

3,4-Dioxybenzaldiketohydrindene, melting at 257°, and prepared by the condensation of protocatechuic aldehyde and diketohydrindene, is a dye (B. 30, 1185). When diketohydrindene is digested alone, or when it is boiled with water, anhydrobisketohydrindene, $C_6H_6(CO)_2C=C<\frac{C_6H_6}{CH_2}>CO$, is formed. This yields intensely colored metallic derivatives. Phenylhydrazine resolves this substance into two molecules of

diketohydrindene-dihydrazone (A. 277, 362). β Methyldiketohydrindene, $C_6H_4(CO)_2CH$. CH_3 , melting at 85°, is prepared from its carboxylic acid, as well as by the rearrangement of ethidene phthalide (p. 286). Methyl iodide converts its sodium derivative into β-dimethyldiketohydrindene, C₆H₄. (CO)₂C(CH₃)₂, which can also be obtained by the action of methyl iodide upon the disodium compound of the diketohydrindene-carboxylic acid. \(\beta\)-Phenyldiketohydrindene, melting at 145°, is made from benzalphthalide, and Bisdiketohydrindene, CaH, (CO)₂CII. CII. (CO)₂C₆II₄, from ethine diphthaly (p. 382). The latter consists of violet-colored needles, melting above 350° (B. 26, 2576; 29, 2376). Potassium per sulphate oxidizes potassium diketohydrindene to diphthalyl ethene, CaH4(CO), C:C (CO)₂C₆H₄, which has been designated indenigo because its structure resembles that of It forms alizarin-red needles, which sublime with decomposition at 200° (B. 30, indigo. 386).

B Acetyl- and Benzoyldiketohydrindene, C,H4(CO)2CH.COR, melting at 110° and 108°, are formed from phthalic esters with acetone and acetophenone. They appear

to be very easily decomposed by alkalies (B. 27, 104).

β-Dichlordiketohydrindene, C₀H₄(CO)₂CCl₂, melting at 125°, is produced by the action of chlorine upon y-oxychlorindone (p. 387). Dilute caustic soda decomposes it quite readily into o-phthalic acid (B. 21, 491, 2380).

Diketohydrindene Carboxylic Ester, C.H. (CO), CH. CO, R, melting at 75-78°. formed from phthalic ester by means of acetic ester and sodium alcoholates, is converted very readily, just like the preceding acid, into diketohydrindene (B. 26, 954).

 β -Methyldiketohydrindene-carboxylic Ester, $C_aH_a(CO)$, $C(CH_a)CO_aR$, is formed

from phthalic ester and propionic ester.

Fluorene is a dibenzopentene resulting from the union of the pentene nucleus with two benzene nuclei. It will be considered in conjunction with chrysene-fluorene and picene-fluorene after the condensed nuclei of the phenanthrene group (pp. 413, 416)—phenanthrene, chrysene, and picene -to which the two first-named bodies are intimately related.

2. NAPHTHALENE GROUP.

Garden (1816) discovered naphthalene, C₁₀H₈, among the distillation products of coal-tar. It shows great similarity to benzene, from which it differs in constitution by C₄H₂. Like benzene, it is produced by the action of intense heat upon various carbon compounds; hence its occurrence in coal-tar. Numerous derivatives are obtained from it by the replacement of its hydrogen atoms; they are very similar to the benzene compounds. Only the most important of them will be considered in the following sections.

CONSTITUTION OF THE NAPHTHALENE NUCLEUS.

The deportment of naphthalene is satisfactorily explained by the formula first suggested by Erlenmeyer, Sr. (A. 137, 346):

It consists of two benzene nuclei, having in common two carbon atoms occupying the ortho position. Graebe (1866) proved the correctness of the formula (A. 149, 20).

The oxidation of naphthalene to o-phthalic acid shows the presence of a benzene nucleus (pp. 36, 239). Further, the oxidation of dichlornaphthoquinone, $C_6H_4:C_4Cl_2O_3$, also yields o-phthalic acid. If, however, dichlornaphthoquinone is converted by PCl₆ into tetrachlornaphthalene, this, upon oxidation, will become tetrachlor-o-phthalic acid. In the second instance, therefore, the benzene nucleus, which in the first case was unattacked, is now oxidized. A perfectly similar method of demonstrain, to which reference has already been made (p. 36), is as follows: Nitronaphthalene, obtained by nitration of naphthalene, yields nitro-o-phthalic acid; whereas amidonaphthalene, resulting from the reduction of the preceding nitronaphthalene, yields o-phthalic acid:

Hence it follows that naphthalene must consist of two symmetrically condensed benzene nuclei. For other formulas, like the *central formula* of Bamberger, the formula of Armstrong, etc., consult B. 23, R. 337, 692; 24, R. 651, 728:

^{*&}quot; Tabellarische Uebersicht der Naphtalinderivate" von Reverdin und Fulda, Basel, Genf, Lyon, 1894.

Isomerisms of the Naphthalene Derivatives.—The isomerisms of the derivatives of naphthalene conditioned by this formula agree with the facts. The substituents are designated according to the diagram:

The replacement of an H-atom in naphthalene can give rise to two isomeric monoderivatives, distinguished as a- and β -derivatives according as the substituent is adjacent

to the complex common to both groups, or separated from it by a CH-group. The positions 1, 4, 5, 8 (a_1, a_2, a_3, a_4) on the one side, and 2, 3, 6, 7 $(\beta_1, \beta_2, \beta_3, \beta_4)$ are equivalent. Liebermann (A. 183, 254) and Atterberg (B. 9, 1736) have adduced proof of the equivalence of the four a-positions. The method adopted is similar to that followed in demonstrating the equal value of the benzene hydrogen atoms (p. 32).

Whether a substituent occupies the a- or β -position is mainly determined by its oxidation to a corresponding o-phthalic acid derivative. Thus, if [1,2,3]-nitrophthalic acid is obtained from a-nitrophthalene, the nitro-group must consequently be adjacent to the contact position of the second benzene nucleus in naphthalene. The constitution of a-oxynaphthalene or a-naphthol is evident also from its synthesis by means of phenylisocrotonic acid, C_8H_5 . CH: CH. CH. COOH (p. 278). Besides, only a-derivatives of naphthalene can be converted into quinones analogous to p-benzoquinone, as these alone possess a free H-atom in the para-position with reference to the substituent. This latter circumstance also determines still other peculiarities in the behavior of the compounds of naphthalene—c, g, the power of the naphthols and naphthylamines to unite with diazobodies, etc. (p. 401).

The disubstitution products of naphthalene, when the substituents are similar, can exist in ten isomeric forms, which are designated by numbers or prepositions (B. 26, R. 533):*

The position of the substituents in the diderivatives can very often be determined by the oxidation method, if thereby it can first be ascertained whether the substituents are in the same nucleus (isonuclear) or in different nuclei (heteronuclear). Isonuclear substitution products with adjacent substituents show in general the same deportment as the ortho-substitution products of benzene, inasmuch as they form similar condensation products (pp. 96, 153, 157, 159). However, a difference appears to exist between positions like 1,2 and 2,3. Thus, only those amidonaphthalenes manifest the ability to form naphthoquinoline rings in which the pyridene-ring can attach itself to $a_n\beta$. C-atoms. It must be assumed that the double linkages in naphthalene are not so easily displaced as in benzene (p. 39). The behavior of the 1,8- or peri-derivatives is remarkable. Like the o-diderivatives, they exhibit a series of hetero-ring formations.

NAPHTHALENE-RING FORMATIONS.

Naphthalene is produced by pyrogenic condensation from a series of carbon compounds, like ethylene, acetylene, ether, etc. Methods of

^{*} In the following diagram the double hexagon of naphthalene is replaced by two parallel lines, as was similarly done with benzene (p. 36).

producing the naphthalene nucleus by processes in which one benzene nucleus pre-exists are more important:

(I) A mixture of benzene and acetylene conducted through a tube heated to redness yields naphthalene (Bull. 7, 306).

(2) It is derived from phenylbutylene, C₀H₅. CH₂. CH₂. CH: CH₂, and its dibromide, on leading their vapors over heated lime:

$$C_6H_6 \xrightarrow{CH_9 - CH_2} CH_2 = C_6H_4 \xrightarrow{CH = CH} + 4H.$$

(3) A direct synthesis of the second benzene ring also ensues in a manner analogous to the formation of the trimethylene and tetramethylene ring, and of the hydrindene ring when o-xylylene bromide acts upon disodium-acetylene-tetracarboxylic ester (Baeyer and Perkin, B. 17, 448).

First, we get the ester of tetrahydro-naphthalene-tetracarboxylic acid, and this by saponification yields tetrahydro-naphthalene dicarboxylic acid. Naphthalene results from the distillation of its silver salt:

$$C_eH_4 {\stackrel{CH_2Br}{<}} + {\stackrel{NaC(CO_2R)_2}{\underset{NaC(CO_2R)_2}{|}}} = C_eH_4 {\stackrel{CH_2-C(CO_2R)_2}{\underset{CH_2-C(CO_2R)_2}{|}}}.$$

(4) What is further noteworthy is the formation of a-naphthol from phenyl-isocrotonic acid when heated (Fittig and Erdmann, B. 16, 43; A. 247, 372; 255, 263; 275, 284; compare formation of indene derivatives, p. 384).

$$C_{\mathbf{g}}H_{\mathbf{5}} \stackrel{CH}{\underbrace{\hspace{1cm}} CH} CH = C_{\mathbf{g}}H_{\mathbf{4}} \stackrel{CH}{\underbrace{\hspace{1cm}} CH} CH = C_{\mathbf{H}} + H_{\mathbf{5}}O.$$
Phenylisocrotonic Acid a-Naphthol.

In a perfectly similar manner 5-, 6-, and 7-chlor-I-naphthols are obtained from o-, m-, and p-chlorphenylparaconic acids; 2- and 4-methylnaphthols from a- and β -methylparaconic acids; a-naphthol-3-methyl ketone (B. 26, 345) from β-benzal-lævulinic acid,

CH — CH. CO. CH₃

OC(OH) — CH₂

OC(OH) — CH₃

when a,γ -diphenylacetoacetic ester, C_8H_8 CH_2 — CO ROCO — $CH(C_8H_8)$, is digested with concentrated sulphuric acid (A. 296, 14).

(5) An interesting formation of a-naphthylamine consists in heating aniline with pyromucic acid and zinc chloride to 300° (B. 20, R. 221):

$$\begin{array}{c} \text{CO}_2\text{H} \cdot \text{C} = = \text{CH} \\ \text{NH}_2 \cdot \text{C}_6\text{H}_5 + \text{O} <_{\text{CH}} = \text{CH} \\ \text{Aniline} \quad \begin{array}{c} \text{Pyromucic Acid} \end{array} = \begin{array}{c} \text{NH}_2\text{C}_6\text{H}_3 <_{\text{CH}} = \text{CH} \\ \text{CH} = \text{CH} \end{array} + \begin{array}{c} \text{CO}_2 + \text{H}_2\text{O}. \end{array}$$

a-Naphthylamine is similarly formed on heating aniline hydrochloride with mannitol

under pressure.

(6) Two molecules of styrolene alcohol or phenyl glycol (p. 248) can be condensed by dilute H_2SO_4 to β -phenylnaphthalene (A. 240, 137):

$$C_8H_8 \nearrow CH(OH). CH_2(OH) \\ CH_2(OH) \stackrel{+}{-} CH(OH)C_6H_5 = C_6H_4 \nearrow CH = CH \\ CH = C. C_8H_5 + 4H_2O.$$

Phenylacetaldehyde is an intermediate product.

(3) When perchlornaphthalene is heated with SbCl₅ to 280-300° it is resol perchlorbenzene, tetrachlormethane and hexachlorethane (B. 9, 1486):

$$C_{6}H_{4} \left\langle \begin{array}{c} CCI = CCI \\ CCI = CCI \end{array} \right\rangle C_{6}CI_{6} + \frac{CCI_{6}}{CCI_{4}} + \frac{CCI_{5}}{CCI_{5}}$$
Perchlornaphthalene.

(4) Decomposition by Reduction in Alkaline Solution.—A ring-decomposition gous to that of salicylic acid (p. 47) is that undergone by 2,1- and 2,3-oxyns acids (p. 408) when their alcoholic solutions are acted upon by metallic sodium (268):

(5) Naphthalene disulphonic acids, naphthylamine- and naphthol-sulphonic containing the substituents in the 1,3-position, sustain a remarkable decompositio o-toluic acid when they are fused with caustic potash (B. 28, R. 364):

$$\begin{array}{c|c} C_{\bullet}II_{\bullet} & C(SO_{3}II) : CH \\ \hline C_{\bullet}II_{\bullet} & CII = -- & C(SO_{3}II) \\ \hline Naphthalene-1-3, disulphonic Acid \\ \hline \end{array} \qquad \begin{array}{c} C_{\bullet}H_{\bullet} & CH_{3} \\ \hline COOH \\ o-Toluic Acid \\ \end{array}$$

m Cresol (Ch. Z. 1895, Nr. 48) is similarly produced on fusing 1,3,6- and naphthalene-trisulphonic acids with caustic potash.

Naphthalene, $C_{10}H_{8}$, melting at 79° and boiling at 218°, occu coal-tar, and is obtained by crystallization from that portion bo from 180-300°. It is purified by distillation with steam and subl tion. It dissolves with difficulty in cold alcohol, readily in hot alc and in ether. It crystallizes and sublimes in shining plates. It is chaterized by its great volatility and possesses a peculiar odor. It for crystalline compound, $C_{10}H_{8}$. $C_{8}H_{2}(NO_{2})_{3}$. OH, with picric acid, we melts at 149° (Fritzsche, J. 1857, 456). m- and p-Dinitrobenzene, nitrobenzene, trinitrotoluene, etc., form similar double compounds.

Naphthalene is applied technically in the preparation of phthalic acid and dye stances. It is also used in carburetting water-gas. It is employed for itch, moths, because of its strong antiseptic properties and its stupefying effect upon the lanimals.

As naphthalene has unsaturated linkages it will, under favorable conditions, tak hydrogen and chlorine: the compounds thus produced will be discussed in conjunc with other hydronaphthalene derivatives at the conclusion of the naphthalene gr Naphthalene, like benzene, is chlorinated, nitrated, and sulphonated by halogen, r acid, and sulphuric acid. See p. 392 for the naphthalene oxidation products.

acid, and sulphuric acid. See p. 392 for the naphthalene oxidation products.

Naphthalene Homologues.—The methylated naphthalenes are present in coal Alkylic naphthalenes also result from the brom-naphthalenes by the action of alkylo and sodium, and from naphthalene by means of alkyl iodides or bromides and Al₂Cl

a. Methyl-naphthalene,
 .
$$C_{10}H_7$$
-a-CH₃
 —20°
 240-243°.

 β. Methyl-naphthalene,
 . $C_{10}H_7$ -β-C $_{11}$
 +32.5°
 241-242° (B. 25, R. 8

 I,4-Dimethyl-naphthalene,
 . $C_{10}H_7$ -β-C $_{11}$
 liquid
 262-264° (B. 28, R. 6

 β-Ethyl-naphthalene,
 . $C_{10}H_7$ -β-C $_{11}$
 —19°
 251°.

 Butyl-naphthalene,
 . $C_{10}H_7$ -β-C $_{11}$

 280° (B. 27, 1623).

 a-Phenyl-naphthalene,
 . $C_{10}H_7$ -β-C $_{11}$
 0°
 325°.

 β-Phenyl-naphthalene,
 . $C_{10}H_7$ -β-C $_{11}$
 102°
 347°.

Potassium permanganate oxidizes ac-tetrahydronaphthylamine to o-hydrocinnam-car-barylic acid (p. 245); ar-tetrahydronaphthylamine, however, because of the oxidation of its amided benzene nucleus, is changed to adipic acid together with oxalic acid (B. 22, 767):

2. Decomposition by Simultaneous Chlorination and Oxidation.—The ring-decompositions, produced by the action of chlorine or hypochlorous acid upon β -naphthoquinone and its derivatives, are very numerous. They proceed in lines analogous to the benzene-ring decompositions. Two groups may be distinguished in these changes: either the naphthalene ring first resolves itself into an indene-ring, which subsequently by decomposition is converted into o-diderivatives of benzene, as in the case of dichlornaphthoquinone (see below), or the break-down proceeds without the intermediate formation of indene, as in the case of β -naphthoquinone or nitro- β -naphthoquinone (see below) (Zincke, B. 27, 2753, etc.). Examples: (a) β -Naphthoquinone, by the action of hypochlorous acid, becomes dioxydiketotetrahydronaphthalene, which by the decomposition of the ring changes to the lactone of o-phenylglycerol-carboxylic acid (p. 264) (B. 25, 3599):

$$\begin{array}{c} C_{\mathbf{c}}H_{\mathbf{c}} \stackrel{CO-CO}{\longleftarrow} \longrightarrow C_{\mathbf{c}}H_{\mathbf{c}} \stackrel{CO-CO}{\longleftarrow} CO \longrightarrow C_{\mathbf{c}}H_{\mathbf{c}} \stackrel{CO-CO}{\longleftarrow} COOH \\ \text{β-Naphthoquinone} \longrightarrow C_{\mathbf{c}}H_{\mathbf{c}} \stackrel{CO-CO}{\longleftarrow} COOH \longrightarrow C_{\mathbf{c}}H_{\mathbf{c}} \stackrel{CO-COOH}{\longleftarrow} CHOII \stackrel{C}{\longleftarrow} CHOII \stackrel{C}{\longleftarrow}$$

(b) With chlorine nitro- β -naphthoquinone first forms a chlorine addition product, which by ring-decomposition readily passes into o- $(a,\beta$ -dichlornitroethyl)-benzoyl formic acid. Chromic acid oxidizes the latter, with loss of hydrochloric acid and carbon dioxide, to nitrochlormethylphthalide, which can be directly formed by treating nitroquinone with chlorine and water (B. 25, R. 732):

$$\begin{array}{c} \text{CO-CO} \\ \textbf{C_8H_4} < \begin{matrix} \text{CO-CO} \\ \text{CH=C.NO_3} \end{matrix} \\ \text{CH=C.NO_3} \\ \textbf{ChCinoperore Addition} \\ \textbf{Chorine Addition} \\ \textbf{Chori$$

(c) Alkalies rearrange 3.4-dichlor- β -naphthoquinone to dichloroxyindene carboxylic acid (p. 386). The latter can be decomposed (1) by changing it to dichlorindone with CrO₃, and tetrachlorhydrindone, the chlorine addition product, when acted upon with alcobolic soda, becomes o-trichlorvinylbenzoic acid; or (2) if the acid be heated to too-lito with oil of vitriol it is converted into β -chlorindone- γ -carboxylic acid. The bromine addition product of the latter acid is decomposed by alkalies with the formation of s-chlorbrom-methylene-homophthalic acid (B. 28, R. 279):

naphthalenes are obtained by the nitration of naphthalenes at high temperature. Consult B. 29, 1243, 1521, for the separation of the 1.5 and 1.5 compound. The 1.5-(a-) compound melts at 216° ; the 1.5-(a-) body melts at 170° , and when heated with potassium cyanide yields potassium naphthalenes, $C_{10}H_{11}N_{10}O_{10}K$. The two distinct or dioxynaphthalenes, when heated with sulphuric acid and reducing agents, form naphthalenes, when heated with sulphuric acid and reducing agents, form naphthalenes (B. 27, R. 959). 1,3-(γ -)-Dinitromaphthalenes, melting it 144°, is obtained from amidodinitronaphthalene. At very low temperatures (—50 b —55°) nitric acid and naphthalene form various dinitronaphthalenes (B. 26, 36). When naphthalene or dinitronaphthalenes are boiled for some time with funds that and sulphuric acids (B. 28, 36') tri- and tetranitronaphthalenes are product. These explode partly with violence on heating.

3. Nitrosonaphthalenes: Mononitrosonaphthalene, C₁₀H₂. NO, seiting # 89° and decomposing at 134°, results from the action of nitrosyl brosside upon me-

cury dinaphthyl.

1,4-Dinitrosonaphthalene is a powder exploding at 120° and is produced when a-naphthoquinone dioxime (p. 406) is oxidized with red pressints of potash. 1,2-Dinitrosonaphthalene, melting at 127° (B. 19, 349; 21, 434), is similarly formed from β -naphthoquinone dioxime.

4. Amidonaphthalenes, Naphthylamines.—(a) Primary amias: The naphthylamines, in contrast to the anilines, are very easily obtained by heating the oxynaphthalenes or naphthols with ammonia-zinc chloride

(p. 72).

a-Naphthylamine, C₁₀H₁-α-NH₂, melting at 50° and boiling at 300°, results from the reduction of α-nitronaphthalene, or on heating α-naphthol with ZnCl₂ or CaCl₂-ammonia to 250°, and is synthetically produced when aniline and zinc chloride are heated with pyromucic acid. It crystallizes in flat needles, which are especially beautiful when they separate from aniline. It acquires a red color on exposure to the air, sublimes readily and possesses a pungent odor. In general, it deports itself perfectly similar to the phenylamines (compare p. 71).

Sodium in amyl alcohol reduces it to a-tetrahydronaphthylamine (p. 411). It is oxidized to a-naphthoquinone when boiled with chromic acid. Oxidizing agents (chromic acid, ferric chloride, silver nitrate) produce an azure-blue precipitate in the solutions of its salts: oxymaph-

thylamine, C₁₀H₉NO (A. 129, 255).

 β -Naphthylamine, melting at 112° and boiling at 294°, results from β -naphthol and ZnCl₂-ammonia. It is odorless and is not colored by ferric chloride and the like. Potassium permanganate oxidizes it to phthalic acid. β -Tetrahydronaphthylamine is formed by its reduction.

Secondary and tertiary naphthylamines: Naphthylakylamines are formed, analogous to the alkyl anilines, from the naphthylamines with alkylogens, or upon heating the naphthylamine hydrochlorides with alcohols: a-Naphthylmethylamine, $C_0H_1NH_1$. Cll₃, boils at 293°; a-Naphthylethylamine boils at 303°; β -Naphthyldimethylamine, $C_{10}H_7$ - β -N(CH₃)₂, melts at 46° and boils at 305° (B. 13, 2053). The Phenylnaphthylamines, $C_{10}H_7$. NH. C_8H_8 , are formed when the hydrochlorides of a- and β -naphthylamines are heated with aniline and zinc chloride. On heating the naphthylamines with zinc chloride or with HCl to 180–190°, or with a- and β -naphthol various dinaphthylamines result. β , β -Dinaphthylamine, $C_{10}H_7$ - β -NH- β - $C_{20}H_{10}$, melting at 171° and boiling at 471°, occurs as a by-product in the tenhical manufacture of β -naphthylamine. Heated to 150° with concentrated hydrochloric acid it heaks down into β -naphthylamine and β -naphthol. Heated with sulphur it forms thiodisaphthylamine, NH($C_{10}H_8$)₂S, corresponding to thiodiphenylamine. When sulphuric acid

(80 per cent.) acts upon β -naphthylamine in the presence of oxidizing agents two naphthalene nuclei unite and naphtidine ($C_{10}H_6$, NH_2), results (B. 25, R. 949) (p. 410).

The acid derivatives of the naphthylamines show great similarity to those of the anilines (see pp. 80-91). The naphthyl benzene sulphamides, C₁₀H₇. NII. SO₂. CaH5, manifest a rather remarkable deportment, similar to that of the naphthols, in that they dissolve in the alkalies, and unite similarly with diazo-salts, etc. (B. 27, 2370). Consult B. 25, R. 9, upon naphthyl carbamine-chlorethyl esters, C₁₀H₇. NH. COOC₂. H₄Cl, and their transposition products. See B. 29, R. 184, for the a-naphthylamine derivatives of succinic, tartaric and citric acids.

Substituted Naphthylumines. - Haloid naphthylamines result by direct substitution, or by the action of ammonia upon substituted naphthols. 1,2- and 1,4-Nitronaphthylamines are formed by the nitration of acet-a-naphthylamine and its subsequent saponification. The 1,4-body melts at 191°. It is exidized to a-naphthoquinone. It forms It forms a-nitronaphthalene by the elimination of the NII, group. Boiling potassium hydroxide converts a-nitronaphthalene into 1,4-nitronaphthol (B. 19, 796; 25, R. 432). The 1,2compound melts at 144°, and yields \(\beta\)-nitronaphthalene (p. 395) and 2,1-nitronaphthol

1-Nitro-2-naphthylamine, melting at 127°, is formed by the nitration of acet- β -naphthylamine and subsequent saponification of the acet-derivative. Nitrous acid and alcohol convert it into a-nitronaphthalene. 2,5- and 2,8-Nitronaphthylamines (B. 25, 2076)

are produced when β-naphthylamine nitrate is introduced into concentrated sulphuric acid.

Naphthylene Diamines.—Diamidonaphthalenes, naphthylene diamines, are obtained by the reduction of dinitro- and nitroamido-naphthalenes, also by the decomposition of amidoazo-naphthalenes, and when dioxynaphthalenes and amido-oxynaphthalenes are heated with ammonia (B. 21, R. 839; 22, R. 42; 26, 188).

The o-naphthylene diamines adapt themselves like the o-phenylenediamines to condensation reactions, in that they form naphtho-derivatives of heterocyclic rings (see p. 95). To a certain degree the o-naphthylene diamines in this respect resemble the 1,8- or peri-

compounds (p. 390).

1,2-Naphthylene Diamine, melting at 98°, is obtained by reduction from β -nitroa-naphthylamine and β -naphthoquinone dioxime (p. 406). 2, 3. Naphthylene Diamine. melting at 191°, is derived from 2,3-dioxynaphthalene by the action of ammonia at 240°. These two bodies yield naphthoazimides with nitrous acid, anhydro bases with carboxylic acids, quinoxalines with o-diketones, etc. (B. 25, 2714; 26, 188; 27, 761). Per fectly similar hetero-ring formations are exhibited by 1,8- (Peri-) naphthylene diamine, melting at 67° and obtained from 1,8-dinitro- or 1,8-dioxynaphthalene; however, it does not, in contrast to the o-diamines, condense with o-diketones, like phenanthraquinones, forming azines (B. 22, 861).

1,3-Naphthylene Diamine melts at 96° (B. 28, 1953). 1,3-(m)-Naphthylene diamine derivatives are derived from naphthylamine sulphonic acids (p. 398), which contain the SO₂H-group in the meta-position with reference to NII₂, by the action of

(1,4)-Naphthylene Diamine, melting at 120°, results from the reduction of a-nitronaphthylamine, and the decomposition of a-amidoazo-naphthalene, by tin and hydrochloric acid. Ferric chloride converts it into a-naphthoquinone, and bleaching lime changes it to naphthoquinone dichlorimide.

See B. 25, 2080, 2082, for 2,5- and 2,8-naphthylene diamines.

5. Diazo- and Azo-compounds of naphthalene: Nitrous acid (or sodium nitrite) act ing upon naphthylamine salts produces naphthalene diazo-derivatives perfectly analogous to the diazo-benzene compounds (p. 99); they yield azo-dyes with the anilines and phenols. β-Diazonaphthalic Acid, C₁₀H₁-β NHNO₂ (p. 99), by rearrangement, yields 2-amido-I-nitronaphthalene (B. 30, 1262).

The azonaphthalenes could not be prepared by reducing nitronaphthalenes. a-Azonaphthalene, $C_{10}H_1N=N$. $C_{10}H_2$, results upon boiling the diazo-compound of amidazo-naphthalene with alcohol. It crystallizes in red needles, or small steel-blue prisms, melting at 190°, and subliming without difficulty. It dissolves with a blue color in concentrated sulphuric acid.

Bensene-azo-naphthalene, Ciell, N. C. H., melting at 65°, has been similarly

o Toluene-azo-naphthalene, $C_{10}H_1$. N_2 . C_7H_7 , melts at 52° (B. 26, 143). Naphthylazoacetic Ester, $C_{10}H_7$. N_2 . $CH_1(COCH_2)CO_2R$, melting at 94°, is formed from diazonaphthalene chloride and sodium acetoacetic ester. Caustic potah changes it to naphthylacetone, and by the acid decomposition it is resolved into metthylasoacetic acid (B. 24, R. 571).

Amido asonaphthalenes: a-Amido-azonaphthalene, C₁₀H₁-a-N₂-a-C₁₀H₆ a₁-NH₂ melting at 175°, is formed by adding sodium nitrite (I molecule) to the aqueous solution of naphthylamine hydrochloride (2 molecules); the diazo-amidonaphthalese, $C_{10}H_7$, N_3 , NII, $C_{10}H_7$ (p. 107), first formed undergoes a molecular rearrangement. Tin and hydrochloric acid resolve a-amidoazonaphthalene into a-naphthylamine and (14)naphthylene diamine. Naphthalene Red belongs to the safranine dyes and is produced when a amidoazonaphthalene is heated with Na-naphthylamine hydrochloride.

/-Amido-azo-naphthalene, from /-naphthylamine, melts at 156° (B. 19, 1282). a-Naphthylamine-azo-benzene Sulphonic Acid, C₆H₄(SO₂H). N₂. C₁₈H₄. NH2, from sulphanilic acid and naphthylamine hydrochloride, is colored orange by caustic potash and red by acids (test for nitrous acid).

The o-azo-compounds of β -naphthylalphylamines, like Benzene-azo- β -naphthylphenylamine, $C_{10}H_6$ [$\begin{bmatrix} 1 \\ 2 \end{bmatrix}N:N:C_6H_5$, when oxidized form ammonium bases of the scuidoscimide group, and when heated they split off aniline, forming naphthophenains (B. 28, 328):

$$C_{10}H_{6} \stackrel{N:N.C_{6}H_{5}}{\underset{N11.C_{6}H_{5}}{\overset{O}{\longrightarrow}}} C_{10}H_{6} \stackrel{N}{\underset{N}{\longrightarrow}} NC_{6}H_{5}; C_{10}H_{6} \stackrel{N:N.C_{6}H_{5}}{\underset{NH.C_{6}H_{5}}{\longleftarrow}} \underbrace{-c_{4}H_{5}NH_{2}}{\underset{NH.C_{6}H_{5}}{\longleftarrow}} C_{10}H_{6} \stackrel{N}{\underset{N}{\nearrow}} C_{4}H_{4}$$

Compare further B. 18, 3132; 20, 1167; 24, R. 765, for the constitution of the preducts resulting from the action of diazo-salts upon B-naphthylamines, which are some times viewed as 3 quinone derivatives.

 III. drawing Derivatives of Naphthalene: Hydrazonaphthalene, C₁₀H₁, NH. NH. C₁₀H₁, melting at 275°, corresponds to hydrazo-benzene. It is formed on boiling azonaphthalene with alcoholic sodium hydroxide and zinc-dust. When digested with hydrochloric acid it changes to the isomeric Naphtidine or diamido-dinaphthyl (com-

pare benzidine, p. 118) (B. 18, 3255). Naphthyl Hydrazines, $C_{10}H_{1}$, NII. NH₂, are derived from the diazo-chloride of the two naphthylamines by the action of stannous chloride and hydrochloric acid (B. 19. R. 303). The a-compound melts at 117°, the β -modification at 125°. They usate with the aldehydes and ketones forming hydrazones; these form naphthindol compounds by condensation, and manifest throughout the tendency to form derivatives and heterring formations similar to those shown by the phenylhydrazines (pp. 123-129) (B. 19, K.

831; 22, R. 672).
7. Sulphonic Acids.—On digesting naphthalene with sulphuric acid we have formed a and β Naphthalene-sulphonic Acids. At lower temperatures (80°) the a-acid, melting at 90°, predominates, while at about 160° and with an excess of sulphane acid the β -acid, melting at 161°, is the chief product. When heated with sulphane acid the a-acid passes into the β -variety. They may be separated by means of the calcium or lead salts. The free acids are crystalline and deliquesce readily. The a acid decomposes upon heating with dilute hydrochloric acid to 200° into naphthaleae and sulphuric acid, whereas the β -acid remains unaltered.

The a sulpho-chloride melts at 66° and boils at 195° (13 mm.). The β sulphe-chloride melts at 76° and boils at 201° (13 mm.) (J. pr. Ch. [2] 47, 49). Protracted heating of naphthalene with concentrated sulphuric acid produces two isomeric disulphe

acids: 2,6- and 2,7-.

Naphthalene Disulphonic Acids.—They are separated by crystallizing their chlorides from benzene (B. 9, 592). Additional disulphonic acids of naphthalene have been prepared by sulphonating the naphthalene monosulphonic acids, by oxidizing thionaphtholsulphonic acids, from the naphthylamine disulphonic acids, etc. A series of naphthalene trisulphonic acids has been made by similar indirect methods (B. 24, R. 654, 707, 15; 27, R. 81; Proc. 126, 168). Chlor-naphthalene Sulphonic Acids have been btained in part by sulphonating the chlornaphthalenes, and in part by replacing the NH₂-roup of the naphthylamine sulphonic acids by halogens (B. 24, R. 658, 707; 25, 2479; 2. 1895, 1114). Nitronaphthalene Sulphonic Acids are obtained by sulphonating the nitronaphthalenes or nitrating the chlorides of the sulphonic acids (B. 26, R. 136).

Some naphthylamine sulphonic acids possess technical value, inasmuch is they form desirable and valuable dyes by combining with the tetrazo-compounds of the benzidine series:

(a) a-Naphthylamine, treated at 130° with an excess of concentrated alphuric acid, forms 1,4-naphthylamine sulphonic acid, naphthionic acid, which can also be prepared from nitronaphthalene with ammonium sulphite by simultaneous reduction and sulphonation (Ch. Z. 1895, 1114). The acid crystallizes with ½H₂O and dissolves sparingly n water. Its sodium salt has the formula C₁₀H₆(NH₂)SO₃Na + 4H₂O. When the acid combines with the tetrazo-derivative of benzidine Congo red is produced. Tin and hydrochloric acid decompose the latter with the formation of 1,2-naphthylenediamine-4-sulphonic acid. See B. 29, 1978, for additional naphthylenediamine-sulphonic acids.

If a-naphthylamine be digested with sulphuric acid at 130° for some time there results, nstead of the 1,4-acid, 1,5-naphthylamine sulphonic acid, naphthalidinic acid, and his tinally gives place to the 1,6-acid (B. 26, R. 534). 1,8- or peri-Naphthylamine Sulphonic Acid is obtained from peri-nitrosulphonic acid. The derivatives of the 1,8-acid show a tendency to part with water with the production of sultams—e. g.: (SO₂H)₂C₁₀H₄ $< SO_2$ (SO₂H)₂C₁₀H₄ $< SO_2$ 1,8-Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 1,8-Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 1,8-Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, NH, 2, NH, 3, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, NH, 3, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, NH, 3, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, Naphsultam, 2,4-disulphonic Acid, (SO₂H)₂C₁₀H₃ $< SO_2$ 1, NH, 2, NH

t.8-Naphsultamtrisulphonic Acid (B. 27, 2137). Peri-Amidonaphthol derivatives are produced when these sultams are fused with caustic potash (B. 28, R. 636).

(b) Four different, isomeric β -naphthylamine sulphonic acids (A. 275, 262) are produced, according to the temperature, when β -naphthylamine is sulphonated:

These acids can also be prepared by the action of ammonia upon the corresponding naphtholsulphonic acids (p. 402). The β- and the F- or acids are particularly valuable, because by their combination with o-tetrazoditolyl beautiful red dyes having a blue tinge result. Certain β-naphthylaminedisulphonic acids are technically important:

See B. 27, 1193, for additional β -naphthylamidopolysulphonic acids. These β -naphthylamine sulphonic acids, which contain a sulpho-group in the m-position with reference to the NH_g-group, readily exchange the sulpho-group for the amine residue when they are heated with amines (B. 28, R. 311).

1.4 Diazonaphthalene Sulphonic Acid, C₁₀H₆ SO₂>O, diazonaphthionic and, is produced by the action of nitrous acid upon naphthionic acid. It forms recellin by combining with a naphthol, and azorubin S by its union with a naphthol a sulphonic

By the union of various azonaphthalene diazo-sulphonic acids—e. g.,

 $C_{10}\Pi_1N_2$, $C_{10}\Pi_3$, $\frac{N_2}{SO_2}>O$ — with naphthol-monosulphonic acid, azo-black dys-

c. g., naphthol black, wool-black, etc.-result.

- 8. Naphthalene Sulphinic Acids are derived by the reduction of the chlorides of salpho-acids. a Naphthalene Sulphinic Acid, C₁₀H₇. SO₂H, melts at 84°, while the 3 acid melts at 105° (B. 26, R. 271). These acids behave just like the benzese so. phinic acids (p. 139) (B. 25, 230). Mixed naphthy! sulphones are prepared from their salts by the action of alkyl bromides (B. 29, R. 979).
- 9. Naphthols: The oxy-derivatives of naphthalene or naphthols in general show a deportment similar to that of the phenols. However, their hydroxyl-group is more reactive. They readily yield naphthylamines with ammonia. They form esters and ethers more easily than the phenols (B. 15, 1427). The naphthols occur in coal-tar (A. 227, 143). a-Naphthol, C10H7-a-OH, melts at 95°, boils at 278-280°, and results from a-naphthylamine by means of the diazo-compound, and upon fusing a-naphthalene-sulphonic acid with alkalies. Its formation from phenylisocrotonic acid (p. 391) is very noteworthy. It is soluble with difficulty in hot water, readily in alcohol and ether, crystallizes in shining needles. has the odor of phenol, and is readily volatilized. Ferric chloride precipitates violet flakes of dinaphthol, C₂₀H₁₂(OH₂), from its aqueous solution. Nitrous acid converts it into 2, 1- and 4,1-nitrosonaphthol (p. 4e6); chloring in acetic acid changes it to various chlorinated naphthols and ketohydronaphthalenes; potassium chlorate and hydrochloric acid oxidiæ it to dichlornaphthoquinone (A. 152, 301); metallic sodium and alcohol reduce it to ar-tetrahydronaphthol (p. 412), while potassium permanganate in alkaline solution breaks it down into carbophenylglyoxylic acid (p.

for the carbonate and phosphate. β-Naphthol, C₁₀H_{7-β}-OH, melting at 122° and boiling at 286°, is derived from 3-naphthalene-sulphonic acid, or 3-naphthylamine. It is readily soluble in hot water and crystallizes in leaflets. Ferric chloride imparts a greenish color to the solution and separates a dinaphthele Nitrous acid and β-naphthol yield 1,2-nitresonaphthol. The acetate $C_{10}H_{7}$ - β - $OC_{2}H_{3}O$, melts at 70°.

See B 28, 3049.

The acetate, $C_{10}H_{1}$ -a-O. $C_{2}H_{3}O_{3}$, melts at 46°.

The bismuth salt of 3 naphthol has been recommended, under the name of orpholess. as an intestinal antiseptic.

Naphthol alkyl ethers are formed when the naphthols are heated with alcohols and hydrochloric acid to 150° (B. 15, 1427).

a Naphthol Ethyl Ether boils at 277°. β-Naphthol Methyl Ether and ethyl ether have been called Jara Jara and Neroline and been used in perfumery (B. 26, 2706). a- and 3-Dinaphthyl Ethers melt at 110° and 106° (B. 13, 1840; 14, 195).

Nuphthel homologues, such as 2,1 and 3,1-methyl naphthol, C10H6(CH3)OH, melting at 80° and 92°, have been prepared from phenyl-a- and -β-methylisocrotonic acids (A. 255-272). 1,4-Dimethyl-3-naphthol, C₁₀H₅(CH₃)₂OH, melting at 136°, is obtained from santonin (p. 432) (B. 28, R. 116, 619).

Substituted Naphthols: Substituted a-naphthols can be synthesized from the substituted phenylisocrotonic acids (compare B. 26, R. 537). Otherwise they are made by methods similar to those adopted with the substituted phenols (p. 148).

Nitronaphthols: 4,1-Nitronaphthol, C₁₀H₆[4](NO₂)[1]OH, melting at 164° and 2,1-nitronaphthol, C₁₀H₆[2]NO₂[1]OH, melting at 195°, result from the oxidation of 4, I - and 2, I-nitrosonaphthol with potassium ferricyanide or nitric acid (B. 25, 973), or by

boiling the corresponding nitronaphthylamines with caustic potash.

2,4-Dinitro-a-naphthol, melting at 138°, is produced by the action of nitric acid upon these nitro-naphthols or upon naphthalene-a-sulphonic acid, a-naphthylamine, and a-naphthol-disulphonic acid (A. 152, 299). It is almost insoluble in water, sparingly soluble in alcohol and in ether, decomposes alkaline carbonates, and forms yellow salts with one equivalent of base. The salts dye silk a beautiful golden-yellow. The sodium salt, $C_{30}H_3(NO_2)_2$. ONa + H_2O , finds use in dyeing, under the name of naphthalene yellow (Martius yellow), and is frequently used to color foods. The potassium salt of dinitronaphthol-sulphonic acid, $C_{10}H_4(NO_5)_3$ $\left\{ \begin{bmatrix} 1 & OK \\ 8 & SO_5K \end{bmatrix}$ (B. 24, R. 709), obtained by the nitration of naphthol-trisulphonic acid, is naphthol yellow.

Trinitro-a-naphthol melts at 177°.

a-Nitro- β -naphthol, melting at 103°, is produced in the oxidation of a nitroso- β -naphthol (p. 406), or from nitro- β -naphthylamine by the action of caustic potash. See **B. 25, 2079,** R. 670, for other nitro- β -naphthols and -naphthol ethers.

Amido-naphthols: These are derived by the reduction of nitronaphthols, by the action of ammonia upon dioxy-naphthalenes, the decomposition of naphtholazo-comounds, etc., etc. In the isonuclear, particularly the 1,3-amidonaphthols, the NH2-group

is more readily displaced than in the hetero-nuclear isomerides. (1,4)-Amido-a-naphthol, $C_{10}H_a(NH_a)$. OH, results from the reduction of (1,4)-nitronaphthol, and by the decomposition of a-naphthol orange, $C_{10}H_a(OH)$. N_2 . C_0H_4 .

SO₃H. It is very unstable. It yields a naphthoquinone by oxidation.

Its ethyl ether, C₁₀H₈(OC₂H₈)NH₂, melts at 96°. 4-Acetamido-1-naphthol, naphthacetol, melting at 187°, is especially well adapted for the production of pure naphtholazodyes (p. 402). 4-Acetamino-1-naphthol Ethyl Ether, naphthacetin, melts at 189° (B. **25.** 3059).

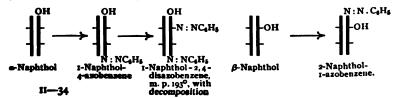
2-Amido-a-naphthol, from 2,1-nitronaphthol, oxidizes in the air to imido-oxynaphthylamine or β naphthoquinonimide, $C_{10}H_{6}$ $\stackrel{O}{\underset{N}{\bigcup}}$ $\stackrel{O}{\underset{N}{\bigcup}}$ $C_{10}H_{6}$ $\stackrel{NH}{\underset{O}{\bigcup}}$, forming violet leaflets.

2,1-Amidonaphthol yields anhydro bases or naphthoxuzoles (see p. 153 and B. 25,

3430) with carboxylic acids, etc.

I-Amido-\beta-naphthol, from the reduction of I-nitro- or nitroso- β -naphthol, or by the decomposition of β -naphthol orange, can be oxidized to β -naphthoquinone. I, 3-Amidonaphthol decomposes at 185° (B. 28, 1952). 1,3-Amido-naphthol decomposes at 185° (B. 28, 1952). 2,3-Amido-naphthol, melting at 234°, is produced by the action of concentrated ammonia at 135-140° (B. 27, 763) upon 2,3 dioxynaphthalene.

Asonaphthols: The naphthols can be readily combined with all diazo-compounds to azo-derivatives. The a-naphthols add the diazo-group as easily to the para (4-) as to the ortho (2-) position. However, the p-position is preferred and it is only when this is occupied that the o-position is assumed (B. 29, 2945; 30, 50). The final products are o,p-disazo-compounds. With the β -naphthols the diazo-group attaches itself only to the a position referred to the OH-group:



These same compounds are also obtained by the action of phenylhydrazine upon the n.iphthoquinones (p. 404). a Naphthoquinone phenylhydrazone is identical with I naphthol 4-azobenzene. 3-Naphthoquinone and phenylhydrazine form a compound which probably is I-naphthol-2-azobenzene, melting at 128°, which cannot be directly made from a naphthol, because it is converted by diazobenzene chloride into 1-naphthol-2,4disazobenzene and in its other deportments justifies the assumption of the presence of a

hydroxyl group (B. 24, 1592; 28, 2414).

The naphthol azo dyes are of great importance in the color industry. They are prepared almost exclusively in the form of their sulpho-acids, which are formed (1) by the union of the naphthols with diazo-sulphonic acids—c. g., a-naphthol orange, OH[1]-C₁₀H₆[1], N₂ · C₆H₄ · SO₂H₄, β-naphthol orange, OH[2]C₁₀H₆[1]N₂ · C₁₀H₈ · SO₂H₄, SO₂H diazonaphthalene sulphonic acid, and sulphobenzeneazobenzene sulphonic acid; (2) by the combination of diazo-salts with naphtholsulphonic acids. Compare B. 29, 2945, for the dyestuffs obtained from naphthacetol and diazo-compounds.

Amidonaphthols, together with amines, are obtained by the reduction of azonaphthols. The benzene azo-p-naphthol ethers, when reduced with SnCl, yield 2-anilide-1,4-anile naphthol ethers, Collis(OR)(NH₂)(NHC₆H₅); the aniline residue enters consequently

into the nucleus (B. 25, 1013); compare semidine rearrangement (p. 118).

(d) Naphthol sulphonic acids have been made in great numbers and introduced into In method of preparation and chemical behavior they exhibit nothing new, when compared with the phenol sulphonic acids (p. 156). In the following paragraph, therefore, a table alone of the representatives of these groups which possess a technical value will be introduced: *

a-Naj^h	thol-	mono-sulphonic Acids:
$C_{10}H_6OH$.	SO,I	I
I	2	Schaeffer's a-acid, A. 152,
	3	^{293.} B. 26 , R. 31.
I	4	Neville and Winther's
		acid, B. 24, 3157; 27, 3458; A. 273, 102.
1	5	L-acid, A. 247, 343.
I	7	B. 22, 993.
1	8	Schöllkopf's acid, A. 247, 306; B. 23, 3088.

a-Naphthel-disulphonic Acids :

C ₁₀ H ₅ OH.	$SO_{3}H$. SO ₃ 1	I
I	2	4	1) isulphonic Acid for Martius' yellow, p. 401.
1	2	7	B. 25, 1400.
I	3	Ś	ε-Disulphonic Acid, B. 22,
1	4	6	3227. D. R. P. 41957.
1	4	7	B. 24, R. 709; 29, 38.
I	4	3	Disulphonic Acid, S, B. 23, 3090.

ß-Naphti	rol-n	nono-sulphemic Acids:
C ₁₀ H ₆ .OH.	SO,	H
2	6	Shaeffer's \(\beta\)-acid, \(A\). 152, 296.
2	8	Crocein Acid, B. 22, 453; 24, R. 654.
2	5	y-Mono-sulphonic Acid, B. 22, R. 336.
2	7	F- or d-acid (compare p. 319), B. 20, 1426; 22, 724.
		22, 724.

β-Naphthol-disulphonic Acids:

C ₁₀ H ₅ OH.	3	6	R-acid, B. 24, 306.
2	3	7	d.Disulphonic Acid, B. 20, 2906.
2	4	8	Disulphonic Acid, C, B. 26, R. 259.
2	6	. 8	G-acid, B. 24, R. 707.

^{*} Compare Nietzki, "Organische Farbstoffe."

(Consult B. 27, 1207, 1209, for other β -naphthol-trisulphonic acids.)

It is the acid of Neville and Winther—of all these acids—which is principally used in the making of azo-dyes. It corresponds to naphthionic acid. It is obtained in its present state by the action of concentrated sulphuric acid upon a-naphthyl carbonate. The R-acid and G-acid also meet with application. They unite with benzene and naphthalene diazo-salts to form a series of *Ponceau*- and *Bordeaux*-dyes of the most varying hues The most important sulphonic acids of β -naphthol are produced together or one after the other in the sulphonation of β -naphthol in the manner represented in the following diagram:

Schaeffer's
$$\beta$$
-Acid R-Acid $\Rightarrow 2,3,6$

$$\{ \Rightarrow 2,8 \Rightarrow 2,3,6 \Rightarrow 2,3,6,8 \}$$
Crocen Acid G-Acid G-Acid

The naphthol sulphonic acids containing an OH- and SO₃H-group in the 1,8 or peri-position give rise to anhydrides having a lactone nature; these are the sultones (compare sultams, p. 399).

Naphsultone, C₁₀H₆ [1]O
Naphsultone, C₁₀H₆ [8]SO₂, melting at 154° and boiling above 360°, is formed
decomposing the diazo-derivative of peri-naphthylamine sulphonic acid. The sultone

by decomposing the diazo-derivative of peri-naphthylamine sulphonic acid. The sultone dissolves in hot alkalies forming salts of perinaphtholsulphonic acid. Sultones have also been obtained from 1,3,8- and 1,4,8-naphtholdi- and 1,3,6,8-trisulphonic acids.

Amidonaphtholsulphonic Acids are produced in the decomposition, by reduction, of the azo-derivatives of naphthol-sulphonic acids, and from nitrosonaphthols by reduction and sulphonation, both of which processes can be worked in common if the nitrosonaphthols be treated with sulphurous acid (B. 27, 23, 3050). In this way 1,2-nitrosonaphthol yields 1,2,4-amidonaphtholsulphonic acid, C₁₀H₅[1]NH₂[2]OII[4]SO₂H. The isomeric 2,1,4-acid, C₁₀H₆[1]OH[2]NH₂[4]SO₃II, produces, even when oxidized in the air, imido-oxynaphthalene-sulphonic acid, SO₃H. C₁₀II₅ NH.

color and is fast to light and alkalies (B. 25, 1400; 26, 1279). The 2,1,6-acid, C₁₀H₅. [1]OH[2]NH₂[6]SO₃H, is used as a photographic developer under the name of *Eikonogen*. Important dyes, from the technical point of view, are 2-amido-8-naphthol-6-aulphonic acids G (B. 25, R. 830; 29, 2267) and 1-amido-8-naphthol-3,6-disulphonic acid H (B. 26, R. 460, 217).

acid H (B. 26, R. 460, 917).

Dioxynaphthalenes.—Nine of the ten possible isomerides are known. The hydronaphthoquinones resulting from the reduction of the naphthoquinones are worthy of nation:

β-Hydronaphthoquinone, $C_{10}H_6[1,2](OH)_3$, melting at 60°, separates when a solution of β-naphthoquinone is boiled with sulphurous acid. It is strongly corrosive. It dissolves in the alkalies with a yellow color, which becomes an intense green upon exposure.

a-Hydronaphthoquinone, C₁₀H_a[1,4](OH)₂, melting at 173°, is obtained from a-naphthoquinone on boiling with hydriodic acid and phosphorus, or with zinc and hydrochloric acid. Chromic acid readily oxidizes it to a-naphthoquinone.

2,3-Dioxynaphthalene melts at 216° (B. 27, 762). Also compare A. 247, 35;

B. 23, 519, etc.

1,3. Dioxynaphthalene, naphthoresorcinol, melting at 1240, is obtained from 1,34 amidonaphtholsulphonic acid. It yields o-toluic acid when fused with caustic potate (see p. 195 and B. 29, 1611).

(see p. 195 and B. 29, 1611).

2-Phenyl-1,3-dioxynaphthalene, melting at 166°, is made by the action of concentral sulphuric acid upon a,7-diphenylacetoscetic ester (p. 391). It absorbs oxygen and changes readily to phenylhydroxy-a-naphthoquinone.

1,7-Dioxynaphthalene melts at 175°; see B. 29, 40; 2,7-Dioxynaphthalene, see B. 30, 1119.

Trioxynaphthalenes.—Two trioxynaphthalenes, a- and β-Hydrojuglones, occur in green walnut shells of Juglans regia (B. 18, 463, 2567). a-Hydrojuglone, C₂H₁ [1.4,5](()H)₃, melting at 169°, is produced by the reduction of juglone. In the ar at 197°, which does not yield juglone upon oxidation. It reverts again to a-hydrojuglone when boiled with dilute alcoholic hydrochloric acid. when boiled with dilute alcoholic hydrochloric acid.

1,2,5,6, Tetraoxynaphthalene, melting at 154°, has been prepared by the reducing

of naphthazarine (B. 28, R. 543).

Thionaphthols have been prepared by the reduction of the chlorides of naphthalese sulphonic acids or from diazonaphthalenes (compare pp. 104, 156). Thionaphthal, naphthyl mercuptan, C₁₀H₁. SH; the α-form is liquid and boils at 286°. The β-variety melts at 81° and boils at 286° (B. 22, 821; 23, R. 327). Phenyl-β-naphthyl Suphide, melting at 51° (B. 24, 2266), is formed when the *lead salt*, (C_BH₇β-S₃Ph is heated, together with brombenzene. Different dinaphthyl sulphides have been prepared by heating the naphthyl-lead-mercaptides. Other methods have been employed in making them (B. 26, 2816). Sulphur chloride and β -naphthol yield dioxydinaphthyl sulphide, $S(C_{10}II_5, OII)_2$, melting at 211°. This can be readily oxidized to a depart C₁₀H₆O compound: S C_{10}^{116} (B. 27, 2993; 28, 114) (compare quinones with two nuclei, p.

Naphthalene disulphydrates, C₁₀H₆(SH)₂; see B. 25, 2735.

(10) Quinones: 1,4- or α-Naphthoquinone corresponds to benzopara-quinone, while 1,2- or \(\beta\)-naphthoquinone corresponds to the orthoquinone of the benzene series, which is only known in certain derivatives.

The same views as those indicated on p. 167 for benzoquinone argue

for the constitution of the 1,4- or a-quinones.

a-Naphthoquinone, $O = [1]C_{10}H_6[4] = O$ or $O[1]C_{10}H_6[4]$, melting at 125°, crystallizes from alcohol in yellow plates, subliming under 100°. It possesses the usual quinone odor and is very volatile in a current of It is formed (1) by oxidizing naphthalene in glacial acetic acid solution with chromic acid; (2) in the oxidation of 1,4-diamido-or 1,4-dioxynaphthalene, 1,4-amido-naphthol (A. 286, 70), a-naphthylamine, etc., with sodium bichromate and sulphuric acid (B. 20, 2283), and (3) when benzeneazonaphthol is treated in the cold with PbO, and sulphuric acid it is decomposed into diazobenzene sulphate and a-naphthoquinone (B. 24, R. 733).

Nitric acid oxidizes a-naphthoquinone to phthalic acid, while a-hydronaphthoquinone is produced in its reduction. See the nitrogen quinone derivatives (p. 406) for its phenylhydrazine and hydroxylamine denva-

tives.

Substituted a Naphthoquinones.—a Naphthoquinone takes up two atoms of chlorine or bromine; the addition products readily part with hydrochloric and hydrobromic acids and hand; and become β -Chlor- and β -Brom- α -naphthoquinones, melting at 117° and 130°.

Hypochlorous acid converts a-naphthoquinone into diketotetrahydronaphthylene oxide, CO - CH >O, which, by the breaking-down of the ethylene oxide union, readily takes up the elements of water, hydrogen chloride and NH2C2H8. The primary addition products sustain the most varied transpositions with great readiness, and form:

exynaphthoquinone, chloroxynaphthoquinone, anilido-oxynaphthoquinone, oxynaphthoqui-

stone anil, and other bodies; compare B. 25, 3599.

Amido-derivatives.—Alkyl- or alphylamidonaphthoquinones are produced on heating primary amines together with a-naphthoquinone: 2-Anilido-a-naphthoquinone, HaO2[2]NH. C6H5, consists of red needles, melting at 191°. 2-Amido-a-naphthoquinone, melting at 203°, is formed together with the isomeric oxy-a-naphthoquimone-imide on boiling amido-a-naphthoquinone-imide (p. 407) with water (B. 27, 3337;

B. 28, 348).

Oxynaphthoquinones. -2-Oxy-a-naphthoquinone, naphthalic acid, C10H5O2[2]OH, selting at 1880, is produced when anilido naphthoquinone (see above) is boiled with dilute sodium hydroxide or oxynaphthoquinone anil (p. 407) with alcohol and sulphuric acid. β -Phenyl- β_1 -oxy- α -naphthoquinone, melting at 147°, is prepared from β -phenyl-1,3-dioxynaphthalene by oxidizing it in alkaline solution with air (A. 296, 18). Iod-oxynaphthoquinone, Iod-naphthalic acid, C₁₀II₄O₄[2]OH[3]I, results from the iodation of naphthalic acid (B. 28, 348). Dyes of the paroxazine- and paradiazine-series exe easily made from the o-oxy- and o-amidonaphthoquinone derivatives (compare also the corresponding naphthoquinone anils p. 407) and o diamines (B. 28, 353).

5-Oxy-a-naphthoquinone, Juglone, consists of yellow needles, melting with decomposition about 150-155°. The best method to obtain it consists in oxidizing a-hydrojugione with ferric chloride. It may be synthetically prepared by oxidizing (1,5)-dioxynaphthalene with chromic acid (B. 20, 934). It dissolves in alkalies with a violet color. Nitric acid converts it into dinitro-oxyphthalic acid (juglonic acid) (B. 19, 164).

Oxy-juglone, Dioxy-a-naphthoquinone, melting with decomposition at 220°, is produced by the oxidation of the alkaline solution of juglone on exposure to the air. An isomeric 5,6-Dioxy-a-naphthoquinone, naphthalizarine or naphthazarine, is formed on heating various a-dinitronaphthalenes with concentrated sulphuric acid in the presence of reducing agents (B. 27, 3462, R. 959; A. 286, 26). It corresponds to alizarine (p. 427), which may be imagined to have arisen from naphthazarine by the addition of a benzene nucleus. It is a valuable mordant dye. Isonaphthazarine is probably a 2,3-Dioxy anaphthoquinone. It is produced from β -naphthoquinone by the action of a little bleaching lime as well as when 2,3-oxyanilido-a-naphthoquinone (see above) is heated with brownine (B. 25, 409, 3606). Carminic acid, the coloring substance of cochineal, is an homologous dioxynaphthoquinone. It can be viewed as 8-methyl-2,6-dioxy-anaphthoquinone (p. 433).

 β -Naphthoquinone, $C_{10}H_6[1,2]O_2$, is produced on oxidizing β -amidoe-naphthol with ferric chloride (B. 17, R. 531; 21, 3472). It consists of red needles, which decompose at 115-120°. It is distinguished from the para-quinones by being odorless and non-volatile. It closely resembles anthraquinone, and especially phenanthraquinone (p. 425); like the latter, it must be considered an ortho-diketone: $C_0 II_4 < \frac{CO \cdot CO}{CO \cdot CO}$.

Like a-naphthoquinone, it can add two atoms of chlorine and bromine, and by the elimination of halogen hydrides Chlor- and Brom- β -naphthoquinones are formed. A little bleaching lime converts β -naphthoquinone into isonaphthazarine (together with various other products, A. 286, 59). This is a dioxy a napthoquinone. Such a rearrangement of 4-oxy- or 4-amido-\(\beta\)-naphthoquinone derivatives into oxy-a-naphthoquimone compounds is a phenomenon that has been frequently observed (compare oxy-anaphthoquinone anil, p. 407). An excess of bleaching lime will produce a rupture in the ring of β -naphthoquinone and convert it into the lactone of o-phenylglycerol carboxylic scid (p. 393).

Similarly, 3-Nitro-1,2-naphthoquinone, melting at 158° and obtained by the attation of Anaphthoquinone, is changed, on treating it with chlorine and water, mu

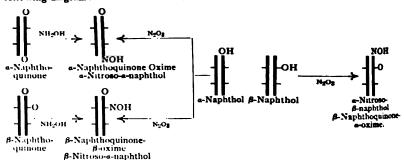
o diderivatives of benzene.

3.4-Dichlor-1,2 naphthoquinone, on the contrary, is first rearranged by alkalies into dichlor-indene oxy-carboxylic acid (p. 393). Potassium permanganate oxidizes 3-aughthouinone to phthalic acid, while sulphurous acid reduces it to 3-naphtholydroquinone (p. 403), and hydriodic acid to 3-naphthol (B. 26, R. 586). Nitrogen Derivatives of the Naphthoquinones.

(1) Naphthoquinone Phenylhydrazones: Unlike the benzene quinones (p. 160), both

the a- and 3-naphthoquinones unite with phenylhydrazine and form phenylhydrazine (ll. 28, 2414), which are, however, to be viewed rather as azo-naphthols.

(2) Nitrosonaphthols or Naphthoquinoximes.—These are produced when the alcoholic solutions of the a- and 3 naphthoquinones are boiled with hydroxylamine hydrochloride, and by the action of nitrous acid upon the naphthols, hence they can be regarded as nitrosonaphthols, $C_{10}H_6(O)(NOH)$ or $C_{10}H_6(OH)(NO)$ (compare nitrosophenols, p. 151). Three isomeric bodies are formed; their relation is expressed by the following diagram:



The three isomerides are weak acids. Oxidation converts them into the correspond-

ing nitronaphthols (p. 401).

" Nitroso " naphthol, "-Naphthoquinone Oxime, melting at 190°, and 3-Nitrosoa naphthol, 3 Naphthoquinone 3 oxime, melting at 1520, are colorless compounds Naphthoquinone oxime is best made from 1-oxy-2-naphthoic acid (p. 408) with nitross acid, when the carboxyl group is split off (B. 26, 1280). a Nitroso-3-naphthol, 3 naphthoquinone-a-oxime, consisting of yellow-brown prisms melting at 106°, precipitates different metals from their salts, and may be used to separate nickel from colul. iron from aluminium, and for the determination of copper (B. 18, 2728; 20, 283). Naphthol green (B. 24, 3741), a wool dye, is the iron salt of a-Nitroso-3-naphthol Sulphonic Acid, $C_{10}H_3(SO_3H)O(NOH)$, obtained by the action of nitrous acid upon Schaeffer's 3-naphthol sulphonic acid (p 402). Consult B. 30, 187, for the product obtained in the action of NO₂-vapors upon Schaeffer's 3-acid.

The ethers of the nitroso naphthols, derived from the silver salts with methyl iodide and partly from the quinones with alkylhydroxylamines, are reduced to amidonaphthols by tin chloride (B. 18, 715, 2225), a proof of the "oxime formula" of the nitrosonaphthols

a-Naphthoquinone Dioxime, $C_{10}II_6$ -1.4-N. OII is formed from a-nitroso-a-naphthol with hydroxylamine hydrochloride. It melts at 207° (B. 21, 433).

 β -Naphthoquinone Dioxime, $C_{10}H_6$ -1,2 $\stackrel{\bullet}{N}$. OH, is derived from β -nitroso-ephthol and from a pieces β naphthol and from a nitroso 3 naphthol by the action of hydroxylamine hydrochloride (B. 17, 2064, 2582). It melts at 149°. After the manner of the glyoximes it forms the anhydride, C₁₀H₆ { [1]N>O, melting at 78°, when digested with alkalies. This com**gound** may also be designated *naphtho-furazane*. The reduction of the dioximes gives rise to naphthylenediamine.

- (3) Naphthoquinone Chlorimides (p. 172): These are made from amido-naphthols, and the dichlorimides from the naphthylene diamines with a bleaching lime solution (B. 27, 238). They resemble the benzoquinone chlorimides, but do not exhibit the same dyestuff condensations as the former (B. 27, 242).
 - a-Naphthoquinone Chlorimide, C₁₀H₈[1,4](NCl)O, melts at 109°. a-Naphthoquinone Dichlorimide, C₁₀H₈[1,4](NCl)₂, melts at 137°.

 β -Naphthoquinone-a-chlorimide, melting at 87°, and β -Naphthoquinone- β -chlorimide, decomposing at 98°, are derived from 2,1- and 1,2-amidonaphthols; they yield β ,a- and α , β -nitrosonaphthols with hydroxylamine. β -Naphthoquinone dichlorimide melts at 105°.

(4) Naphthoquinone-imides and Anils: The indophenol and indo-aniline dyes of the naphthalene series belong in this group,—e. g., a-Naphthol Blue or Indophenol, C₁₀H₆[1]O[4]N.C₆H₄N(CH₃)₂,—which results when naphthol interacts with dimethyl-p-phenylenediamine or nitrosodimethyl aniline. The simple a-naphthoquinone-imide is not known. 2-Amido-1,4-naphthoquinone-imide, diimidonaphthol, C₁₀H₅[2]NH₂[1]O[4]NH (A. 154, 303), is produced in the oxidation of 1-0xy-2,4-diamidonaphthalene. Boiling water changes diimidonaphthol to 2-0xy-1,4-naphthoquinone-imide, melting at 195° (B. 23, 2454); aniline to 2-anilido-1,4-naphthoquinone anil, C₁₀H₅[2]NHC₆H₅[1]O[4]NC₆H₅, melting at 187° (B. 13, 123; 21, 391, 676); with hydroxylamine an oxynaphthoquinone oxime, which consists of two modifications, red and yellow, which can be changed one into the other (B. 29, 1415). 2-Oxy-1,4-naphthoquinone anil, melting at 240° with decomposition, is produced by the action of aniline in the cold upon β-naphthoquinone-4-sulphonic acid, the oxidation product of 1,2-amidonaphthol-4-sulphonic acid. This is an instance of the rearrangement of a β- into an a-naphthoquinone derivative. The p-diamines react in a manner similar to aniline, so that in this way hydroxyl indaniline does (see above) can be obtained (B. 27, 25, 2050)

that in this way hydroxyl indaniline dyes (see above) can be obtained (B. 27, 25, 3050).

a-Naphthoquinone-phenyldiimide, C₁₀H₆(NH)(NC₆H₅), melting at 129°, is formed upon oxidizing p-amidonaphthylphenylamine with mercuric oxide (A. 286, 186).

β-Naphthoquinone-imides, also called *imido-oxy*- or *imidoketone naphthalenes*,—e. g., C₁₀H_g-1,2-O(NH) (pp. 401, 403),—are produced when the alkaline solutions of the 1,2-amidonaphthols are oxidized with air.

11. ALCOHOLS OF THE NAPHTHALENE SERIES AND THEIR OXIDATION PRODUCTS.

A. Alcohols: Naphthobenzyl Alcohols, Naphthyl Carbinols, $C_{10}H_7$. CH_2 . OH_4 , the a- melting at 60° and boiling at 301° , and the β - melting at 80° , result when their amines are treated with nitrous acid (B. 21, 257). The naphthobenzyl chlorides, $C_{10}H_7CH_2Cl$, the a- boiling at 178° (25 mm.) and the β - melting at 47° , are formed when chlorine acts upon the two methyl naphthalenes (p. 394) at a boiling temperature (B. 24, 3928). Naphthobenzylamines, menaphthylamines, $C_{10}H_7$. CH_2 . NH_2 , the a-boiling at 292° and the β - melting at 60° , have been made by the reduction of the corresponding naphthoic acid thiamides, as well as of the naphthonitriles.

B. Aldehydes, Ketones. When the naphthyl methyl alcohols are oxidized, the products

 α -Naphthaldehyde, $C_{10}H_7$. CHO, boiling at 291°, and β -Naphthaldehyde, melting at 59° (B. 20, 1115; 22, 2148).

a Naphthyl-methyl Ketone, Acetonaphthone, C₁₀II₇. CO. CH₃, is derived from naphthalene and acetyl chloride by means of aluminium chloride. It melts at 34° and boils about 295°. Its chloride splits off hydrogen chloride and becomes a-naphthyl acetylene, C₁₀H₇. C: CH. Potassium permanganate oxidizes the ketone to a-naphthyl glyoxylic acid, C₁₀H₁CO. COOH, melting at 113°, which is also formed by the saponification of naphthol cyanide obtained from a-naphthyl chloride. By reduction it becomes a-naphthyl acetic acid, C₁₀H₇. CH₂. COOH, melting at 131°. I-Naphthol-3-methyl Ketone, C₁₀H₆[1](OH)[3](CO. CH₃), melting at 174°, is formed from β-benzal-kevulnic acid by condensation (p. 391 and B. 24, 3201). See B. 28, 1946, for 1,2-naphthol methyl ketone.

C. Naphthalene Monocarboxylic Acids:

a. Naphthoic Acid, C10H7-a-CO2H, melting at 160°, is derived from a-naphthonitrile by saponification (B. 20, 242; 21, R. 834); by fusing a-naphthalene sulphonic acid with sodium formate; by the action of sodium on a mixture of a-brom-naphthalene and chlor-carbonic esta; and from naphthalene, urea chloride, and aluminium chloride (B. 23, 1100). β-Naphthoic Acid, melting at 182°, is formed from β-naphthonitrile (B. 24, R. 725), as well as by the oxidation of \(\beta\)-alkylnaphthalenes (B. 17, 1527; 21, R. 355). Both acids are decomposed when heated with baryta into CO, and naphthalene.

Homelogous Naphthalene Carboxylic Acids: a Naphthyl-acetic Acid, Cally+ ('H, . COOII, melting at 131°, has been made by the reduction of a-naphthyl glyanyte acid (p. 407), while the A acid, melting at 139°, has been prepared by means of the cyanide from 3 naphthobenzyl chloride (B. 29, 2373).

3-Phenyl- and 3 Naphthyl-a-naphthoic Acids are the chrysenic and pices and

(see chrysene and picene, p. 416).

Substituted Naphtheic Acids: The nitration of a naphthoic acid produces 1,5 and 1,8 nitronaphthoic acids, melting at 239° and 275° respectively. Boiling nine and converts them into 1.5 (a) and 1,8 (b) dinitronaphthalene (p. 396). 1,4-Nitronaphthose acid, melting at 220°, results upon saponifying the nitrile, which is formed on treating the diazo derivative of 1,4-nitronaphthylamine with potassium cuprous cyanide.

Ferrous sulphate and ammonia reduce the 1,5-acid to a stable amido-naphthoc acid (1.5), melting at 212° (B. 19, 1981), whereas the same reagents reduce the 1.8 acid to (1,8) or peri-amido-naphthoic acid, which when free, passes like the La amido sulphonic acids (p. 399), quite readily into its inner anhydride, Naphthostyril. $C_{10}H_{6} \stackrel{f}{=} \stackrel{f}{=}$

See B. 24, R. 037, for the nitro 3 naphthoic acids. 2,3-Amido-naphthoic Acid. melting at 2147, results upon treating the corresponding oxy-naphthoic acid with ammora

Oxynaphthole Acids, Naphthol Carboxylic Acids, containing the OH- and COOHgroups in the ortho-position, are prepared like the orthophenol carboxylic acids-i.e. if

heating the solium naphtholates with CO₂ under pressure.

1.2 (a) Naphthol Carboxylic Acid, $C_{10}H_{6}[1](OH)[2](COOH)$, melting at 1867.8 formed from a naphthol, and from 3-naphthol-sodium with carbon dioxide and presser at 120-145°; 2,1 (3) Naphthol Carboxylic Acid, melting with decomposition at 150°. is similarly produced, while if A naphthol-sodium be heated more strongly, 200-250°, in a current of carbon dioxide, the product will be 2,3 naphthol carboxylic acid, melting at 210° The 2, 1/(3) naphthol carboxylic acid is distinguished by the easy mobility of its carboxylic group. Heated alone, or when boiled with water, it changes to B-naphthol; nitrous and converts it into a nitroso-3-naphthol (see p. 406 for method of preparation), and disc benzene salts into benzene azo 3 naphthol, etc. The 2,3-acid, on the other hand, is ver stable, and resembles salicylic acid. Because of its striking and remarkable yellow color

the formula of a ketodihydronaphthoic acid, $C_6H_4 \sim CH_2 = C$. COOH, has been proposed for this acid. The behavior of the acid toward phenylhydrazine supports this view: it is very probable that at first a hydrazine is produced, which subsequently, owns to indol condensation, forms a phenonaphtho-carbazole-carboxylic acid (B. 29, 265).

Naphthoxanthones, C10H6 CO C10H6 (B. 25, 1642), are produced when the three

o naphthol carboxylic acids are heated with acetic anhydride.

(1.8) or peri Naphthol Carboxylic Acid is derived from (1,8)-amido-naphthoc acid by means of the diazo-compound. It breaks down into water and its y-lactoric $C_{10}H_6\left\{\begin{bmatrix} 1\\8\end{bmatrix}CO\right\}$, melting at 169°.

- 2,3-Oxynaphthoic acid and diazobenzene chloride yield a mixed azo-compound. Reduction converts this into 1,2,3-amido-oxynaphthoic acid, which, on boiling with sulpharic acid, becomes 1,2,3-dioxynaphthoic acid. This can also be obtained from β -naphthohydroquinone and carbon dioxide, and by oxidation it is changed to β -naphthoquinone-carboxylic acid (B. 28, 3089). Consult B. 29, 39.
- D. Naphthalene Di- and Poly-carboxylic Acids: Six of these acids are known. It is remarkable that the 1,8- or peri-acid, so called naphthalic acid, C₁₀H_e[1,8](COOH)₂, is produced by the oxidation of acenaphthene (p. 410), and also from its half-nitrile, which is made by saponifying the diazo-derivative of peri-amidonaphthoic acid. The following diagram represents the relations of a series of peri-naphthalene derivatives:

Just as in the case of other peri-derivatives, so here naphthalic acid when heated to 180° breaks down without melting into water and its anhydride, C₁₀H₆(CO)₂O, melting at 266°, which like phthalic anhydride condenses with phenol to phenol-naphthalcin,

C₂H₄OH)₂ (B. 28, R. 621). Compare B. 28, 360, for naphthal-imide, -anil, and -phenylhydrazil. 1,2-Naphthalene Dicarboxylic Acid, obtained by the saponification of its nitrile, melts at 175° and passes into its anhydride, melting at 105° (B. 25, 2475). 1,5-Naphthalene Dicarboxylic Acid, B. 29, R. 516.

Naphthalene Tetracarboxylic Acid, C₁₀II₄[1,4,5,8](CO₂H)₄, with the carboxyl groups in the two peri-positions of naphthalene, results when pyrenic acid is oxidized

(B. 20, 365).

Naphthonitriles, Cyan-naphthalenes: Naphthonitriles may be obtained by the distillation of the alkali salts of the naphthalene disulphonic acids, or the phosphoric esters of the naphthols with potassium cyanide or yellow prussiate of potash (B. 21, R. 834).

the naphthols with potassium cyanide or yellow prussiate of potash (B. 21, R. 834).

a-Naphtho-nitrile, a-Cyan-naphthalene, C₁₀H₇. CN, melting at 37° and boiling at 298°, has also been prepared from formnaphthalide, C₁₀H₇. NH. COH, as well as from a-naphthalene diazochloride by means of copper and potassium cyanides.

from a-naphthalene diazochloride by means of copper and potassium cyanides.

\$\beta\$-Cyan-naphthalene melts at 66° and boils at 304°. 1,2-Dicyan-naphthalene.

\$C_1H_[1,2](CN)_2\$, melting at 190°, is produced when 1,2-chlornaphthalene sulphonic acid is distilled with potassium ferrocyanide (B. 25, 2475). For additional isomeric discrepancy paththalenes see A 152, 280; I 1860, 482, etc.

dicyan-naphthalenes see A. 152, 289; J. 1869, 483, etc.

12. Dinaphthyl- and Dinaphtyl-methane Derivatives: Different isomeric dinaphthyls have been made by conducting the vapors of naphthylene through tubes heated to redness, by heating naphthalene with Al_{Cl_0} , or from brom-naphthalene and sodium, and by heating mercury dinaphthyl, $IIg(C_{10}H_{1})_{3}$, etc. (B. 28, R. 184).

The diamidodinaphthyls or naphtidines, corresponding to the benzidines or dis diphenyls, result from the rearrangement of the hydrazonaphthalenes, or directly from the naphthylamines by the action of 80 per cent. sulphuric acid in presence of oxidate, such as ferric oxide, etc. (B. 25, R. 949). Similarly, naphthols and ferric chloride yield

dinaphthols.

Disaphthylmethane derivatives, like a-dinaphthol methane, $CH_1(C_{10}H_0 \circ OH)_p$ and ethidene-a-dinaphthol, CH_1 . $CH(C_{10}H_0 \circ OH)_p$, have been made by the condenstion of naphthols with aldehydes. The products from the latter and β -naphthol ready part with water and become xanthenes, hence they in all probability contain the akylidene groups in the o-position with reference to the hydroxyls: β -Dimaphthol methant, melting at 190°, yields, with POCl₃, dinaphthoxanthene, C₁₀H₆ CH₂>C₁₀H₆ while benzaldehyde and \$ naphthol at once form ms-phenylnaphthoxanthene, CaHaCH(CaHa)0 (B. 25, 3477; 26, 83), together with an acetal (see I, p. 200).

13. Acenaphthene: Acenaphthene, or peri-Ethylene Naphthylene, C₁₀H₁ [[1]CH₁] melting at 95° and boiling at 277°, is a peculiar derivative of naphthalene, which is obtained by conducting a-ethyl naphthalene through a red-hot tube, or by the action of alcoholic potash upon a-brom-ethyl naphthalene, $C_{10}H_7$. C_7H_6 Br. It also occus is coal tar. Inasmuch as acenaphthene is oxidized by sodium bichromate and sulphure acid to naphthalic acid (p. 409) the side-chain C_2H_4 must be arranged in the two peripositions (I and 8) of naphthalene. Acenaphthene-quinone, $C_{10}H_6(CO)_p$, melting at 261°, is a by-product in this oxidation. Zinc-dust and acetic acid reduce it to acenaph-

tenone, C10 Ha. CH2. CO, melting at 121°, while hydriodic acid and phosphorus change it to bisacenaphthylidene, (C₁₀H₆.CO.C:)₂, melting at 294°, and alkalies decompose it into naphthaldehydic acid (B. 26, R. 710; A. 290, 195):

$$C_{10}\Pi_{6} \stackrel{C}{\underset{CO}{\downarrow}} = C_{10}\Pi_{6}$$
Bisaccenaphthylidene
$$C_{10}\Pi_{6} \stackrel{C}{\underset{CO}{\downarrow}} = C_{10}\Pi_{6} \stackrel{CO}{\underset{CO}{\downarrow}} + C_{10}\Pi_{6} \stackrel{CH(0H)}{\underset{CO}{\downarrow}} \rightarrow C_{10}\Pi_{6} \stackrel{CH(0H)}{\underset{C}{\downarrow}} \rightarrow C_{10$$

When the vapor of acenaphthene is conducted over lead oxide heated to redness two atoms of hydrogen split off and acenaphthylene, C₁₀H_e CH results. This forms mi low plates (p. 419) (B. 26, 2354), melts at 92° and boils at 270° with decomposition Chromic acid also oxidizes it to naphthalic acid.

14. Hydronaphthalene Derivatives.

Hydronaphthalene compounds attach themselves to naphthalene just as the hydroaromatic benzene derivatives did to benzene. Naphthalene and its derivatives take up hydrogen and the halogens more readily than the compounds of benzene. Those naphthalene derivatives which have added hydrogen to one nucleus alone are remarkable and interesting because they manifest in one substance the differences which prevail between an aromatic and a hydroaromatic or alicyclic nucleus. While the non-hydrogenized nucleus of the respective naphthalene compounds retains the aromatic properties, the hydrogenized alicyclic nucleus assumes, on the contrary, the nature of a fatty radical, and as a consequence the

whole system acquires the character of an homologous benzene derivative (Bamberger, A. 257, 1).

Ī

ľ

A. Dihydronaphthalene Derivatives: Dihydronaphthalene, C₁₀H₁₀, melting at 15° and boiling at 212°, is formed when naphthalene is reduced with sodium in a boiling ethyl alcohol solution. The entering hydrogen atoms assume the 1,4-position, because the hydride yields o-phenylene diacetic acid when it is oxidized. It can be viewed as the hydrocarbon of a-naphthoquinone if the latter be considered as a diketone. **Dihydron**aphthalene resembles the olefines—e. g., ethylene—in that it readily takes up two univalent atoms or radicals. Thus with bromine it forms a dibromide, with hypochlorous acid a glycolchlorhydrin (p. 412). Tetrahydronaphthylene oxide (p. 412) can be easily obtained from the latter and is capable of rearranging itself to 1,2-dihydro- β -maphthol, $C_{10}H_{10}O$, boiling at 162–168° (28 mm.), which may be oxidized to dihydroisocommarin-carboxylic acid (p. 392), and when it splits off water naphthalene is produced

Naphthalene Dichloride, $C_{10}H_8Cl_2$, is a yellow oil formed when naphthalene is treated with potassium chlorate and hydrochloric acid. It changes to a-chlornaphthalene at 40-50°, and by the elimination of hydrogen chloride.

Dihydronaphthoic Acids: Sodium amalgam reduces the a- and β -naphthoic acids, two hydrogen atoms being added to the nucleus already carrying the carboxyl-group, and in the cold there result unstable, and when heat is applied stable, dihydronaphthoic acids, $C_{10}H_9 \cdot CO_2H :$

a-Stable melting at 125°;
$$\beta$$
-stable melting at 161°. a-Unstable " 91°; β -unstable " " 104°.

The unstable pass into the stable modifications on boiling them with caustic soda. Potassium permanganate oxidizes the stable a-acid to hydrocinnamic acid, while the unstable acid yields oxalic acid and phthalic acid. The dibromide of the unstable β -acid, in contrast with the stable modification, readily changes to a brominated lactone. All these facts point to the following formulas for the stable a- and the unstable β -acid (A. 266, 169):

The dihydro- β -acids, when oxidized with potassium ferricyanide, revert again to

B. Tetrahydronaphthalene Derivatives: Tetrahydronaphthalene, C₁₀H₁₂, boiling at 206°, is formed in the reduction of naphthalene with sodium in amyl alcohol ing at 200°, is formed in the reduction of naphthalene with sodium in amyl alcohol solution; also from ar-tetrahydronaphthylamine by the elimination of the NH₂-group; hence the H-atoms are only present in the one nucleus. Naphthalene Tetrachloride, C₁₂H₂Cl₄, melting at 182°, is produced when chlorine is conducted into a chloroform solution of naphthalene. Boiling alcoholic potash changes it to dichlornaphthalene (p. 395). See B. 28, R. 392, for the oxidation of naphthalene tetrachloride. Consult B. 24, R. 713, for the chlorine addition products of chlorinated and sulphur-containing maphthalenes. Naphthalene Tetrabromide melts at 111° (C. 1897, I, 984).

The naphthylamine and naphthol hydrides are particularly interesting. Sodium acting upon the boiling amyl alcohol solution of the naphthols and naphthylamines causes these bodies to add four hydrogen atoms, each to one nucleus. If the latter carries the NH.

bodies to add four hydrogen atoms each to one nucleus. If the latter carries the NH₂er OH-group, the body formed no longer possesses the character of a naphthylamine or a naphthol, but has that of a benzene homologue, amidated or bearing the OH group in the side chain. Should, however, the non-substituted nucleus be hydrogenized, then the products acquire the nature of homologous anilines or phenols. E. Bamberger, who birst observed these relations and explained them, designated the second class of temhydro-derivatives as aromatic (ar-), and the first class as aliphatic-cyclic or alicyclic (ac-):



ac-Tetrahydroa-naphthylamine



ar-Tetrahydroβ-naphthol



ar-, ac-Tetrahydro-1,5-naphthylene Diamine.

a Naphthylamine and a naphthol upon reduction yield ar-tetrahydro-a-naphthylamine and naphthol, while the β-compounds form both the ar- and the ac-tetrahydro-derivative; the latter predominates. 1,5-Naphthylamine diamine yields ac-, ar-tetrahydro-naphthylamine, which, by elimination of the aromatic NH₂ group, forms ac-tetrahydro-a-naphthylamine:

ar Tetrahydronaphthylamines, NH_2 , C_0H_3 : (C_0H_0) . The α -body boils at 275° and the β -form at 276°. They are feeble bases and form diazo- and azo-compounds. They exercise a reducing power with salts of the noble metals. By oxidation with pota-

sium permanganate all yield adipic acid and oxalic acid (p. 393).

Chromic acid oxidizes the a-compound to ar-tetrahydro-a-naphthoquinone, C_0H_1 : $C_2:(C_4H_2)$, melting at 55°, which in every respect resembles benzoquinone—c. c, like the latter, it does not form a hydrazone with phenylhydrazine (compare p. 406). Tetrahydronaphthylamines, $C_aH_4:(C_4H_7:NH_2)$; the a-body boils at 246° and the a- at 240°. They are strong bases, which absorb carbon dioxide from the air. They do not form diazo-derivatives. Potassium permanganate ruptures the hydrogenized ring and produces o-cinnam-carboxylic acid.

ac. ar-Tetrahydro-1,5-naphthylene Diamine, NH₂. C₅H₅: (C₄H₇NH₂), melting at 261°, combines in itself both the properties of an aromatic and of an alicyclic amine. It contains an asymmetric carbon atom, and has been resolved into a

dextro- and a Levo-modification.

ar Tetrahydro-a-naphthol, OH. C₆H₃: (C₄H₈), melting at 69° and boiling at 265°, is also derived from ar tetrahydro-a-naphthylamine by means of the diazo-derivative.

ac Tetrahydro 3-naphthol, C₆H₄: (C₄H₇OH), is an oil, boiling at 264°. It exhibits the character of a fatty alcohol and resembles similarly constituted camphor alcohol, like menthol and borneol (pp. 313, 324).

A series of tetrahydronaphthalene derivatives has been obtained, starting with diby

A series of tetrahydronaphthalene derivatives has been obtained, starting with different dronaphthalene: Thus, phenol and the latter form Tetrahydronaphthylphenol, $C_6H_4:(C_4H_7,C_5H_4OH)$ boiling at 130° (B. 24, 179), while bromine changes it to dihydronaphthalene dibromide, $C_6H_4:(C_4H_6Br_2)$. Boiling potassium carbonate converts the latter into Tetrahydronaphthylene Glycol, $C_6H_4< CH_2$ —CHOH melting at 135°, which by oxidation is broken down into o-phenylene diacetic acid. It is an analogue of ethylene glycol. The chlorhydrin (above), $C_{10}H_{10}Cl(OH)$, melting at 117°, with caustic potash yields Tetrahydronaphthylene Oxide, $C_{10}H_{10}O$, melting at 43° and boiling at 258°, which manifests all the chemical properties of ethylene oxide (i. 298). Bases have converted the chlorhydrin into a series of "alkines," of which mention may be made of—

Trimethyl-oxytetrahydronaphthylene Ammonium Hydroxide,

 $C_{6}H_{4} < CH_{2}$. CHOH

CH₂. CHN(CH₃)₂OH, because of its intimate connection with choline (1, 309). The feebler alkalies convert this oxide into the isomeric β -ketotetrahydronaphthalene, $C_{6}H_{4} < CH_{2} - CH_{2}$, melting at 18° and boiling at 138° (16 mm.), which can also be

prepared by the distillation of o-phenylene propionacetic acid (p. 394) (B. 28, 745). It behaves like a fatty ketone (B. 27, 1547) with sodium bisulphite, phenylhydrazine, and hydroxylamine. The chlorine addition products of the naphthoquinones are diketotetra-hydroxaphthalene derivatives. They readily part with hydrogen chloride and thus yield substituted naphthoquinones (pp. 404, 405). Diketotetrahydronaphthylene Oxide, Commonthylene City (COmmonthylene), is produced by the action of bleaching lime upon

a-maphthoquinone (p. 404 and A. 286, 71).
ac-Tetrahydronaphthoic Acids are also classified into aromatic and alicyclic. ar-Tetrahydro-a-naphthoic Acid, COOH. C₆H₈: (C₆H₈), with an amide melting at 182°, is derived from its nitrile, a rearrangement product from ar-tetrahydro-a-naphthalene diazo-

chloride and potassio-copper cyanide.

ac-Tetrahydronaphthoic Acids, the a- melting at 85° and the β - at 96°, are formed when naphthoic and dihydronaphthoic acids are reduced with sodium amalgam. They resist the action of potassium permanganate more strongly than the dihydro-acids. In comparison with the latter they thus prove themselves to be saturated acids. The long-continued action of the oxidant finally changes them to phthalic and oxalic acids (A. 202).

ac-Tetrahydronaphthalene Dicarboxylic Acid, $C_6H_4[C_4H_6(CO_2H)_2]$, melts at 199°, with the production of its anhydride, melting at 184°. The latter is also formed on heating potassium tetrahydronaphthalene tetracarboxylate, the ester of which has been synthesized from o-xylylene bromide and the sodium derivative of the dimalonic acid ester (p. 301) (B 17, 448). Tetrahydro-1,5-naphthalene Dicarboxylic Acid melts

ester (p. 391) (B 17, 448). Tetrahydro-1,5-naphthalene Dicarboxylic Acid melts at 238° (B. 29, R. 517).

C. Hexa-, Octo-, Deca-, and Dodeca-hydronaphthalenes, C₁₀H₁₄, C₁₀H₁₆, C₁₆H₁₆, and C₁₆H₂₆, boil at 200°, 185-190°, 173-180°, and 153-158° respectively. They have been obtained by the action of hydriodic acid and phosphorus upon naphthalene

(B. 16, 796, 3032; Å. 187, 164).

3. PHENANTHRENE GROUP.

Phenanthrene occurs, together with anthracene, in coal-tar and in the so-called "stubb," a mass of substance obtained (together with fluoranthene and pyrene) in the distillation of mercury ores in Idria. It is prepared synthetically (1) (with diphenyl, anthracene, and other hydrocarbons) from various benzene compounds, by conducting their vapors through a red-hot tube—e. g., from toluene, stilbene, diphenyl, and ethylene, and particularly from dibenzyl and o-ditolyl:

(2) Sodium acting on o-brombenzylbromide also produces it (together with anthracene, p. 421):

(3) It also appears in the condensation of coumarone with benzene (B. 23, 85):

$$\begin{array}{c} C_6H_4-CH \\ I \\ COMMATONE \end{array} + C_6H_6 \xrightarrow{\qquad \qquad } \begin{array}{c} C_6H_4-CH \\ C_6H_4-CH \\ C_6H_4-CH \\ Phenanthrene. \end{array}$$

Chrysene is similarly formed from commarone and naphthalene, and amidonaphthalene (p. 391) from furfurane and aniline.

4. When the diazo-derivative of o-amido-a-phenylacetic acid is acted upon with copper powder phenanthrene carboxylic acids (B. 29, 496) result:

This reaction recalls the formation of diphenyl from benzene and diazobenzene, as well as that of diphenylketone from the diazo-derivative

of o-amidobenzophenone (p. 347).

Phenanthrene in accordance with these methods of production must be viewed as a derivative of diphenyl, in which two ortho-positions of the two benzene rings are joined by the group CH = CH, which therefore constitutes, with the four carbon atoms of the two benzene rings, a third normal benzene ring:

$$CH = CH$$

The oxidation of phenanthrene leads to a similar conclusion. Phenanthraquinone is the first product, and by continued oxidation it yields diphenic acid or diphenyl-o₂-dicarboxylic acid (p. 340):

$$\begin{array}{c|c} C_6H_4 \cdot CH & C_6H_4 \cdot CO \\ C_6H_4 \cdot CH & C_6H_4 \cdot CO \\ \end{array}$$

$$\begin{array}{c|c} C_6H_4 \cdot CO_2H \\ C_6H_4 \cdot CO_2H \\ \end{array}$$

$$\begin{array}{c|c} C_6H_4 \cdot CO_2H \\ \end{array}$$

Phenanthrene, C₁₄H₁₀, crystallizes in colorless plates, melting at 99°. and boiling at 340°. It dissolves readily in ether and benzene; but with more difficulty in alcohol and water. The solutions exhibit a blue fluorescence.

The picric acid compound, $C_{14}II_{10}$. $C_9H_2(NO_9)_3$. OH, separates in yellow needles, melting at 144°. Consult A. 196, 34; B. 19, 761, for a method of isolating phenanthropic forms and the second s

threne from crude anthracene.

Hydrogen addition products result upon heating phenanthrene with hydriodic acid and phosphorus. The Tetra-hydride, C₁₄H₁₄, boils at 314°. The Per-hydride, C₁₄H₂, boils at 270-275° (B. 22, 779). Chlorine produces substitution products, of which the octo-chloride, C₁₄H₂Cl₈, melts at 270-280°, and by further chlorination is split into tion, yielding the dibromide, C₁₄H₂B₁. Bromine combines with phenanthrene in CS₂ solubromphenanthrene, C₁₄H₂B₁. This melts at 63°, and is oxidized to phenanthraquinone Nicet acid. Nitric acid converts phenanthrene into three nitrophenanthrenes, which yield three

amido-phenanthrenes, C₁₄H₂(NH₂), by reduction.

Two phenanthrenes, C₁₄H₂(NH₂), by reduction.

Phuric acid. If these be distilled with yellow prussiate of potash we obtain two cyanido, yielding the corresponding carboniling acids: a-Phenanthrene Carboxylic Acid, yielding the corresponding carloxylic acids: a-Phenanthrene Carboxylic Acid,

CO₂H₁ . C₆H₃ . CH : CH . C₆H₄, which melts at 266°, and is oxidized to phenanthraquinone carboxylic acid, while the β -acid, C_8H_4 . CH: $C(CO_9H) = C_8H_4$, melting at 251°, yields phenanthraquinone. See above for the synthesis of this acid.

Phenanthraquinone, $(C_6H_4)_2(CO)_2$, is formed in the action of chromic acid upon phenanthrene in glacial acetic acid solution; most readily by heating it with a chromic acid mixture (A. 196, 38). It crystallizes in long, orange-yellow needles, melts at 198°, and distils without decomposition. It dissolves readily in hot alcohol, ether, and benzene, but sparingly in water. It dissolves in concentrated sulphuric acid with a dark green color, and is reprecipitated by water. By adding toluene containing thiotolene and sulphuric acid to the acetic acid solution of phenanthraquinone a bluish-green coloration is produced (see thiophene).

In deportment it recalls β -naphthoquinone. It is odorless, not volatile in steam, unites with one and two molecules of hydroxylamine, and

is not reduced by sulphurous acid.

Phenanthraquinone-monoxime, C₁₆H₈O(N.OH), consists of golden yellow needles, melting at 158°. If it is heated together with glacial acetic acid and hydrochloric acid to 130° it sustains the transposition of ketoximes (p. 341), and forms diphenimide (B. 21, 2356):

$$C_6H_4-C:NOH \longrightarrow C_6H_4-CO$$
NH.

 $C_8H_4-C:NOH \longrightarrow C_8H_4-CONH.$ The dioxime forms an anhydride, $C_{14}H_8 \stackrel{N}{\swarrow} N$ O, melting at 181°. This is a furazane

derivative.

Phenanthraquinone, being an o-diketone, forms phenazine derivatives with o-diamines. See B. 24, R. 630, 631, for the condensations of acetoacetic ester and acetone. By oxidation with chromic acid, or by boiling with alcoholic potash, phenanthraquinone is oxidized to diphenic acid; ignition with soda-lime produces diphenylene ketone (p. 419), fluorene (p. 417), and diphenyl. Diphenylene glycollic acid (p. 419), fluorene alcohol, and diphenylene ketone are obtained on boiling with aqueous soda-lye. Ignited with zincdust we obtain phenanthrene.

When phenanthraquinone is digested with concentrated sulphurous acid it is reduced to Phenanthrene-hydroquinone, Dioxyphenanthrene, $\begin{bmatrix} C_0H_4-C(OH) \\ T_0H_4-C(OH) \end{bmatrix}$. This can also be obtained by the reduction of the chloride of diphenic acid (p. 341). With hydriodic acid phenanthraquinone forms Phenanthrone, $C_8H_4 - CH_2$ and with hydriodic acid and phosphorus in glacial acetic acid solution it yields—

Monacetyl-dioxyphenanthrene, $(C_6H_4)_2$ COOC₂H₃, which on heating condenses to Tetraphenylene Furfurane, $\begin{pmatrix} C_6H_4-CH-CH-C_6H_4 \\ C_6H_4-CH-CH-C_6H_4 \end{pmatrix}$ (B. 26, R. 585). When

a mixture of phenanthraquinone and aldehydes is exposed to sunlight a union follows with the production of monacidylphenanthrene hydroquinones (A. 249, 137) (compare 1, 75). Retene or Methyl Isopropylphenanthrene, $(CH_3)(C_3H_7)C_6H_2$ CH: CH

melting at 98° and boiling at 394°, is a homologue of phenanthrene.

Retene occurs in the tar of highly resinous pines, and in some mineral resins. It is isolated from those portions that boil at elevated temperatures. Its picric acid compound forms orange yellow needles, melting at 123°. Chromic acid in glacial acetic acid solution oxidizes retene to retene quinone, C₁₈H₁₈O₂ (methyl isopropyl phenanthraquinus, melting at 197°. It resembles phenanthraquinone in its entire deportment. Solim hydrate converts retene quinone into-

Retene Diphenic Acid, C₁₈H₁₆<CO₂H, and Retene Glycollic Acid, C₁₈H₈.C (OH). CO.H. Potassium permanganate oxidizes retene quinone to diphenylen kean dicarboxylic acid (p. 419) and retene ketone, CH₃. (C₃H₇). C₄H₂ CO (B. 18, 1027)

1754, R. 558). 1754, N. 550.

Retene Dodecahydride, dehydrofichtelite, C₁₈H₂₀, is an oil, boiling at 336°. It is formed when retene is heated with hydriodic acid and phosphorus to 250°, and also in the action of iodine upon fichtelite, C₁₈H₂₀, melting at 46°, which occurs, together with retene, in the peat of fossil plants (B. 22, 498, 635, 780, 3369).

Chrysene and picene possess a structure similar to that of phenanthrene. They can be derived from phenylnaphthalene and dinaphthyl the same as phenanthrene from diphenyl:

The constitution of these bodies is deduced mainly from the products of their oxidation. Chromic acid first changes them to chrysoquinone and picenoquirone, which can be further transposed into chrysene and picene ketones, chrysenic acid and picenic acid. 3 phenylnaphthalene and β-dinaphthyl:

Chrysene, C_{1} , II_{12} , m. p. 250° and b. p. 448°, consists, in a pure condition, of silver white leatlets with a violet fluorescence. When impure it has a yellow color (hence the boiling points. It can be synthesized from phenyl-naphthyl-ethane, C_6H_3 . CH_4 . CH_1 . $C_{10}II_{11}$, just as phenanthrene is produced from dibenzyl (p. 413); also by beating naphthalene with coumarone. It is formed in large quantities by heating indene (p. 384); $2C_9II_8 = C_{18}H_{12} + 4II$ (B. 26, 1544). See B. 24, 949, for substituted chrysenes. The hydrides, $C_{18}II_{28}$, b. p. 360°, and $C_{18}H_{30}$, m. p. 115° and b. p. 353° (B. 22, 135), result upon heating chrysene with hydriodic acid and phosphorus.

When discrete dwith chromic acid and algorial acid acid stream ovidings to so called

When digested with chromic acid and glacial acetic acid chrysene oxidizes to so called Chrysoquinone, C18 II 10 02 (a diketone), which crystallizes in red needles, melting at

235°

Chrysoketone, C17H10O, results when chrysoquinone is distilled with lead oxide.

Hydriodic acid and phosphorus reduce it to chrysofluorene, C17H12

Chrysenic Acid, $C_{17}II_{19}O_3$ (β -phenylnaphthyl carboxylic acid), is produced when chrysene is fused with caustic alkali. When this acid loses CO_3 it becomes 3-phenyl-

naphthalene (B. 26, 1745). Picene, C₂₂II₁₄, is the hydrocarbon with the highest melting point (364°). It is formed by the distillation of lignite, coal-tar, and petroleum residues. It can be synthesized from naphthalene and ethylene bromide by means of Al₂Cl₄ (B. 24, R. 963). It is very sparingly soluble in most of the solvents, but most readily in crude cymene. When heated to 250° with hydriodic acid and phosphorus, Picene Perhydride, CnH

is produced. It melts at 175°. Picene is oxidized by chromic acid to an orange-red quinons, $C_{22}H_{12}O_{31}$, which, like chrysene, is changed on the one hand to picene ketone, picene fluorene alcohol, and picene fluorene, $(C_{10}H_{4})_2CH_3$, and on the other to picenic acid or dinaphthyl-carboxylic acid and β -dinaphthyl (B. 26, 1751).

4. FLUORENE GROUP.

Just as phenanthrene, chrysene, and picene were regarded as symmetrical o₁-ethylene derivatives of diphenyl, phenylnaphthyl, and dinaphthyl, so fluorene, chrysene-fluorene, and picene-fluorene may be viewed as oz-methylene derivatives of the last-mentioned hydrocarbons, and accordingly may be designated diphenylene methane, phenylene naphthylene, and dinaphthylene-methanes. Fluorene is also closely allied to diphenylene oxide, diphenylene sulphide, and diphenylene-imide or carbazole (see this), dibenzo-derivatives of furfurane, thiophene, and pyrrol:

$$\begin{array}{c|cccc} C_6H_4 & CH_2 & C_6H_4 & C$$

General Methods of Formation:

1. Fluorene is formed by conducting vapors of diphenylmethane through tubes heated to redness; chrysofluorene is similarly obtained from β -naphthyl phenylmethane:

$$(C_6H_5)_2CH_2 \longrightarrow (C_8H_4)_2CH_2.$$

2. o-Diphenyl carboxylic acid, phenylnaphthyl carboxylic acid or chrysenic acid, and dinaphthyl carboxylic or picenic acid, when heated alone or in the form of salts, yield fluorene, chrysene, and picene ketones, which can be readily reduced to fluorene, chrysofluorene, and picene-fluorene; conversely, the acids are reformed when the ketones are fused with caustic potash:

$$\begin{array}{cccc} C_{g}H_{4} \cdot COOH & \longrightarrow & C_{g}H_{4} \\ & \longleftarrow & C_{g}II_{4} \end{array} \\ CO.$$

3. Fluorene ketone is also obtained from the diazo-derivative of o-amidobenzophenone by the elimination of nitrogen; similarly, chrysene ketone is formed from o-amidophenyl-a-naphthyl-ketone (B. 29, 826):

$$C_6H_4$$
-N₃OH C_6H_5 -> C_6H_4 - CO

4. Phenanthraquinone, chrysoquinone, and picenoquinone, when oxidized, also yield the ketones of the corresponding fluorenes:

Fluorene, Diphenylene Methane, C₁₃H₁₀, m. p. 113° and b. p. 295°, crystallizes in colorless leaflets with a violet fluorescence. It forms a compound with picric acid, melting at 81°. It results upon exposing diphenyl methane to a high heat (above), and in the reduction of diphenylene ketone with zinc dust or upon heating it to 160° with 111 and phosphorus. The chromic acid mixture oxidizes it to diphenylene ketone.

Methylhexahydrofluorene, boiling at 128° (14 mm.), results from the action of $\Gamma_1 \circ_5$ upon methylbenzylcyclohexanol, the reduction product of benzylidene-methyl cyclohexanon, (CH₂)(OH)C₆H₂: CH₂. C₆H₄ - CH₂)C₆H₄. CH₂. C₆H₄ (B. *) 2002), produced in the condensation of benzaldehyde and methyl-cyclo-hexanon.

Retene-fluorene, methylisopropyldiphenylenemethane, (CH3)(C3H7)C4H2 CH, meth Retene-fluorene, methylisopropylaiphenylenemethane, CH₂, method ing at 92°, is derived from its ketone upon distillation with zinc-dust. Chrysofluorene,

naphthylene-phenylene-methane, C10H6-CH2-C6H6, melting at 180°, is derived from 3 henzylnaphthalene or from chryso-ketone. An isomeric isochryso-fluorene, melting at 70°, is obtained from a benzylnaphthalene (B. 27, 953). Picene-fluorene, paylomethane, (C10 II 6)2 CII2, melting at 306°, is produced on heating its ketone to 160-175° with hydriodic acid (A. 284, 70).

Diphenylene-phenylmethane, ms.-Phenyl-fluorene, $(C_6H_4)_2$ CHC₆H₅, melting at 140°, results on heating triphenylmethane chloride, $(C_6H_5)_3$ CCI, or potassium triphenylmethane (p. 351); from fluorene alcohol, benzene, and sulphuric acid (B. 22, R. 660), and by distilling hydrofluoranic acid (p. 362) over soda-lime.

Diphenylene-diphenyl-ethane, $(C_6H_4)_3$ CH. CH(C₆H₅)₂, melting at 217°, and Diphenylene-diphenyl-ethylene, $(C_6H_4)_3$ C: C(C₆H₅)₂, melting at 229°, arise in the

 $(C_6H_4)_2$. C. ĆO

ing at 256°, one of the reaction-products of cold concentrated sulphuric acid spon benefits acid (p. 369). Diphenylene-diphenyl-sthylene is products. ben ilic acid (p. 369). Diphenylene-diphenyl-ethylene is produced on heating benzopenone chloride with fluorene. It consists of colorless crystals, the solutions of which are conved intensely yellow. The moderated oxidation of this body with chromic acid gives rise to diphenylene-diphenyl-pinacoline, melting at 172°. Its structure is unsumetrical: $(C_6H_4)_2C(C_6H_5)CO$. C_6H_6 , because it is decomposed by alcoholic causes. potash into diphenylene phenylmethane and benzoic acid. It also results from potassium

triphenylmethane and benzoylchloride (B. 29, 2152).

Bidiphenylene Ethane, $(C_6H_4)_2$ CH, $CH(C_6H_4)_2$, colorless needles, melting at 246°, is produced, together with bi-diphenylene Ethylene, bifuorene, $(C_6H_4)_2$ C:C $(C_6H_4)_2$, melting at 188°, on heating fluorene with lead oxide. The second hydrocarlon is also formed on heating fluorene with bromine, chlorine, or sulphur. It consists of beautiful red colored needles. Its bromine addition product is colorless, and when heated with sodium in xylene solution it reverts to the red hydrocarbon (B. 25, 3142) A. 290, 238; 291, 1). The following diagram is interesting from the point of view of

the color of highly condensed hydrocarbons:

$$C_6H_5$$
 C_6H_5
 C_6H_5
 C_6H_5
Tetraphenylethylene
(p. 378). Colorless

Colorless; yellow in solution

Compare the yellow color of acenaphthylene (p. 410). Chromic acid oxidizes be diphenylene ethylene into a pinacoline, melting at 258° (together with fluorenone), which probably, like diphenylene-diphenyl pinacoline, possesses an unsymmetrical structure corresponding to the formula C_6H_4)₃: $C - C_6H_4$, because, like the diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-diphenylene-di

pinacoline, it is resolved by alcoholic potash into the acid $(C_6H_4): CH - C_6H_4 \cdot C_6H_5 \cdot COOH$. The pinacoline is also produced in the reduction of fluorenone with zinc-dust and acetyl chloride. It is further identical with the bidiphenylene-ethine oxide (B. 29. 2152; A. 291, 1), produced on heating bidiphenylene-ethine dibromide with water.

Fluorene Alcohol, 16H₄ CII. OII, melting at 153°, results in the action of sodium amalgam upon diphenylene ketone and by heating sodium diphenylene glycollic acid to 120°. Concentrated sulphuric acid or P2O5 colors it an intense blue, and produces Huorene ether, (C13H2)2O, melting at 290°.

tetene-, chrysene-, and picene-fluorene alcohols, melting at 134°, 167°, and respectively, are obtained by methods similar to those pursued in the preparation morene alcohol.

Diphenylene Ketone, Fluorenone, C₆H₄>CO, melting at 84° and boiling at 341° ay, R. 641), is obtained from diphenic acid, isodiphenic acid, and o-diphenyl carplic acid when heated with lime; by oxidizing fluorene with a chromic acid mixture, by heating phenanthraquinone with caustic lime (A. 196, 45; 279, 257), and when diazo-compound of o-amido-benzophenone (p. 347) is heated with water (B. 28, 111). **acid** on fusion with potassium hydroxide. Its oxime, $(C_6H_4)_3C$: NOH, melts at 193° p. 420); the phenylhydrazone melts at 151° (B. 29, 230, R. 26).

letene Ketone, (C₃H₇)(CH₃)C₄H₂.CO.C₄H₄, melts at 90°. Chrysoketone. [a. CO. C₁₀H₆, melts at 130°. See p. 418 for the production from o-amidophenyl-a-bthyl ketone. Picene Ketone, (C₁₀H₆)₂CO, melts at 185°.

-Oxydiphenylene Ketone, Oxyfluorenone, CaH3(OH). CO. CaH4, melting at 115°, btained from sym. o-diamidobenzophenone (p. 347) on boiling its diazo-salts with r. It forms yellow-red or dark-red alkali salts, which manifest a feeble dye nature. In forms yenow-red or dark-red aikin saits, which mainest a feeble dye nature.

In fused with caustic potash it decomposes into o-phenylsalicylic acid, C₈H₅. C₆H₅-[]COOH, which is recondensed by concentrated sulphuric acid to oxydiphenylene has been been concentrated and the concentrated of the concentration of the anthridone (B. 28, R. 455):

$$c_6H_3(NH_2)-CO-c_6H_4 \longrightarrow c_6H_3-NH-CO-c_6H_4$$

h also results by Beckmann's transposition on heating the oxime of fluorenone with chloride (B. 29, 230):

$$c_{eH_4-C:(NOH)-c_{eH_4}} \longrightarrow c_{eH_4-NH:CO-c_{eH_4}}$$

arboxylic Acids: Diphenylene Acetic Acid, Fluorene Carboxylic Acid, (C.H.), . CO.H, melting at 221°, results on reducing diphenylene glycollic acid with hydriodic and phosphorus.

iphenylene Glycollic Acid, ms-Oxyfluorene Carboxylic Acid, (C6H4)2C(OH).CO3melting at 162°, is produced when phenanthraquinone is boiled with sodium oxide. In this instance an atomic rearrangement occurs, similar to that observed he transition of benzil to benzilic acid, or of β -naphthoquinone to oxyindene car-

$$|H_6CO \xrightarrow{H_2O} C_6H_6 C(OH). COOH \qquad C_6H_4 - CO \xrightarrow{C_6H_4} C_6H_4 C(OH)COOH.$$

t is decomposed by concentrated sulphuric acid or upon heating, when carbon dioxide water split off and fluorene ether results. Chromic acid oxidizes it to diphenylene ne. Analogues of diphenylene glycollic acid have been obtained from retene- and sene-quinone (above).

Diphenylene-ketone Carboxylic Acids, C₆II₄. CO. C₆II₃. CO₂H. The a-acid, ing at 191°, is produced by the oxidation of fluoranthene with a chromic acid mix-

. Sodium amalgam converts it into a-fluorenic acid, CaHa. CHa. CaHa. CoaH,

melting at 245°, which yields fluorene if it be distilled with zinc dust. Isodiphe results when it is fused with potassium hydroxide (p. 341), while heating wi

breaks it down into carbon dioxide and diphenylene ketone.

The β -acid is formed upon heating diphenylene-ketone dicarboxylic acid; it coryellow needles that sublime without melting. The γ - or ortho-acid is formed diphenic acid is heated. It melts at 223°. Fusion with caustic potash chang diphenic acid (B. 20, 846; 22, R. 727).

phenic acid (B. 20, 846; 22, R. 727).

Diphenylene-ketone Dicarboxylic Acid, C₈H₄ CO, results when retene-c

C₈H₄ (CO₂H)₉

A sulphyr-vellow, crystalline powder,

is oxidized with potassium permanganate. A sulphur-yellow, crystalline powder, above 270° breaks down into carbon dioxide and β -diphenylene-ketone carboxyli It yields diphenyl when distilled with lime. Diphenylene-ketone is produced fr silver salt.

Fluoranthene and pyrene, occurring in the "stubb fat" of Idrialso found with the condensed hydrocarbons just mentioned in the boiling fractions of coal-tar.

Fluoranthene, $C_{15}H_{10}$, Idryl, melts at 110°. Its picric acid compound melts at Fluoranthraquinone, $C_{15}H_{8}O_{2}$, is obtained by oxidizing idryl with chromic aci melts at 188°, and may be further oxidized (with the elimination of CO_{2}) to a-diphenylene-ketone carboxylic acid.

The constitution of fluoranthene and of fluoranthoquinone probably corresponds formulas (A. 200, 1):

Pyrene, $C_{16}H_{10}$, melts at 148° and boils at 260° (60 mm.). The picric acid pound melts at 222°. Chromic acid oxidizes it to Pyrenquinone, $C_{16}H_{9}O_{2}$.

Pyrenic Acid, $C_{15}Il_8O_5$, results upon further oxidation of pyrenquinone. It ketone-dicarloxylic acid. It forms an anhydride or imide compound quite re (B. 19, 1997). When pyrenic acid is distilled with lime, it forms Pyrene Ket $C_{12}Il_8(CO)$, melting at 141°. Potassium permanganate oxidizes pyrenic acid 1,4,5,8-naphthalene tetracarboxylic acid (p. 409), and pyrene ketone to naphthalic. For the constitution of pyrene consult B. 20, 365; A. 240, 147.

5. ANTHRACENE GROUP.

Anthracene (from $\tilde{a}\nu\theta\rho a\xi$, carbon), occurring together with the meric phenanthrene in the high-boiling portions of coal-tar, is the par substance of a large group of bodies to which a series of vegetable coapounds, and in particular the very important dye (alizarine, purpur, etc.) of madder-root belong. The anthracene derivatives can be view as diphenylene compounds, in which two phenyl groups are linked gether by two C-atoms occupying the ortho-positions with reference one another:

$$C_{\bullet}H_{\bullet} \xrightarrow{CH_{2}} C_{\bullet}H_{\bullet} \xrightarrow{O} C_{\bullet}H_{\bullet} \xrightarrow{CH} C_{\bullet}H_{\bullet} \xrightarrow{CH} C_{\bullet}\Pi_{\bullet} \xrightarrow{O} C_{\bullet}H_{\bullet} \xrightarrow{CO} C_{\bullet}H_{\bullet}$$
Dihydroanthracene
Diphenylene-o,o-dimethylene
Diphenylene-o,o-diketone.

Dihydroanthracene, when heated or when oxidized, loses two atoms of hydrogen, and becomes anthracene. When this occurs it may be supposed that a mutual union of the two methylene carbon atoms takes place (see, however, B. 24, R. 728).

Synthetic Methods for the Production of Anthracene Derivatives:

1. Anthracene may be formed from benzene, acetylene tetrabromide, and Al₂Cl₄ (B. 16, 623).

2. It is also produced from methylene bromide, benzene, and Al₂Cl₆. Dihydroanthracene is the primary product, but it loses two atoms of

hydrogen, and anthracene results.

3. Further, dihydroanthracene, and subsequently anthracene, is obtained (together with toluene) from two molecules of benzyl chloride on heating it with aluminium chloride or with water to 200° (Limpricht, 1866), when dibenzyl will also be produced.

Anthracene may also be derived from diphenylmethane with Al₂Cl₆. It is very probable that the diphenylmethane is first resolved into benzyl chloride and benzene. Unsym. diphenylethane in an analogous manner yields ms-dimethylanthracene (B. 27, 3238).

4. Finally, dihydroanthracene is obtained from two molecules of o-brombenzyl bromide by the action of metallic sodium (B. 12, 1965) (compare p. 413):

(1)
$$C_{6}H_{6} + \frac{BrCHBr}{BrCHBr} + C_{6}H_{6}$$

(2) $C_{6}H_{6} + \frac{BrCH_{2}Br}{BrCH_{2}Br} + C_{6}H_{6}$

(3) $C_{6}H_{6} - \frac{CH}{2CI} + \frac{CH}{C_{6}H_{6}}$

(4) $C_{6}H_{6} - \frac{CH}{2CI} + \frac{CH}{BrCH_{2}} + \frac{CH}{C_{6}H_{6}} + \frac{CH}{C_{6}$

Anthraquinones are obtained (5 a) by the action of zinc-dust upon the chloride of phthalic acid and benzene. (5 b) Similarly, oxyanthraquinones are produced on heating phthalic anhydride with 1 mol. of a mono- or polyhydric phenol and sulphuric acid to 150°. If there is an excess of phenol present, phthaleins result (p. 363). (6) o Benzoyl-benzoic acid and P₂O₅ yield anthraquinone on the application of heat. (7) Di- and tetra-oxyanthraquinones are formed when metaoxy- and dimetadioxybenzoic acids are heated with sulphuric acid (p. 222):

The methods just given and a series of others—e.g., the production of anthr from o tolylphenyl ketone and lead oxide, and that of anthracene and methy cene from o tolylphenylketone and o-ditolylketone by means of zinc-dust (B. 23, F demonstrate the accepted symmetry of the derivatives of anthracene, which i proved by the following fact: brominated o-benzoylbenzoic acid from o-phth (p. 350) yields bromanthraquinone; the oxyanthraquinone obtained from th however, can be oxidized to o-phthalic acid; so that both in the synthesis and position of the molecule o-phthalic acid appears, which, in the first instance, nected with the one and in the second case with the second half of the molecule pare constitution of naphthalene, p. 389) (B. 12, 2124):

$$\operatorname{Br}: C_{\mathbf{6}}H_{\mathbf{5}}\left\{ \begin{bmatrix} \mathbf{1} \end{bmatrix} CO: C_{\mathbf{6}}H_{\mathbf{5}} \longrightarrow OII: C_{\mathbf{6}}H_{\mathbf{5}}\left\{ \begin{bmatrix} \mathbf{1} \end{bmatrix} CO[\mathbf{1}] \\ \mathbf{2} \end{bmatrix} C_{\mathbf{6}}H_{\mathbf{4}} \longrightarrow \frac{\operatorname{HOOC}[\mathbf{1}]}{\operatorname{HOOC}[\mathbf{2}]} \right\}$$

Therefore, anthraquinone and anthracene, genetically connected with it, have metrical constitution corresponding to the symbols:

Anthracene is a nucleus resulting from the condensation of three benzene nu which the intermediate or middle member shows a para-union. The positions S(u) are alike; also 2, 3, 6, 7 (β -). By the replacement of the middle hydrogen at anthracene) derivatives or messe-derivatives are obtained. In contrast with the substituents of the two outer benzene nuclei are designated by the prefix benz. I of the anthracene transpositions the intermediate C-atoms are first attacked.

Anthracene, C₁₄H₁₀, melting at 213° and boiling at 351°, is iso with tolane (p. 371) and phenanthrene (p. 413), and is produced acing to the methods indicated upon p. 421. (See also B. 28, R. 148 is found in large quantities in coal-tar.

Crude anthracene, boiling at 340-360° and beyond, is best purified by treating i liquid sulphurous acid, which chiefly takes up the admixtures (B. 26, R. 634). If ditional methods of purification see B. 18, 3034; 21, R. 75; A. 191, 288. Cically pure anthracene is prepared by heating anthraquinone with zinc-dust.

Anthracene crystallizes in colorless monoclinic tables, showing a be ful blue fluorescence. It dissolves with difficulty in alcohol and e but easily in hot benzene. Pieric acid unites with it, yielding $C_{14}F_{C_6}H_2(NO_2)_3OH$, crystallizing in red needles, and melting at 138°.

When the cold saturated solution of anthracene in benzene, or, better, in xylene (1 R. 547), is exposed to sunlight, a dimolecular modification of anthracene, Para-an cone, $(C_{14}H_{10})_2$, separates out in plates. It dissolves with difficulty in benzene, i attacked by nitric acid or bromine, melts at 244°, and in so doing reverts to cor anthracene.

Alkylic Anthracenes: (a)
$$C_6II_4 \stackrel{CH}{\stackrel{C}{\leftarrow}} C_6H_3R$$
; (b) $C_6H_4 \stackrel{CR}{\stackrel{C}{\leftarrow}} C_6H_4$

Benz-alkyl Derivatives ms- or γ -Alkyl Derivatives.

(a) The benz-mono-alkylic anthracenes can exist in two isomerides (a- and β -). Methyl Anthracene, $C_aH_a(CH)_aC_6H_3$. CH_3 , melting at 190°, occurs in anthracene, and resembles anthracene. It is obtained on conducting the vapor ditolyl-methane and ditolyl-ethane through a red-hot tube; also on heating er

and chrysophanic acid (hydroxylmethyl-anthraquinones) with zinc-dust, as well as by srolonged boiling of benzoyl xylene, C_6H_5 . CO. C_6H_9 (CH₃)₂. Concentrated nitric scid converts it into Methyl-anthraquinone. Anthraquinone-carboxylic acid is pro-Inced when methyl-anthracene, dissolved in glacial acetic acid, is oxidized by chromic

Benz-dimethylanthracenes, $C_{14}H_8(CH_3)_2$, melting at 200° and 225°, are obtained irom xylyl chloride, and from toluene and CH_2Cl_2 by means of Al_2Cl_3 , according to methods 2 and 3 (p. 421). A dimethyl anthracene has been isolated from the high-

soiling aniline oils.

(b) Meso- or γ-Alkyl Anthracenes are obtained from the alkylic hydranthranols, C₆H₄<CR(OH)>C₆H₄, by the elimination of water. This happens on boiling them with alcohol, hydrochloric acid, or picric acid (A. 212, 100). Alkylic oxanthranols are formed upon oxidation: γ-ethyl, isobutyl, and amyl anthracenes, melting at 60°, 57°, and 59°. γ -Phenyl anthracene, $C_{14}H_9(C_6H_5)$, melting at 152°, is obtained from phenyl anthranol (p. 424) with zinc-dust.

7-Dimethyl Anthracene, C₆H₄(C. CH₃)₂C₆H₄, melting at 179°, is derived from its dihydride, the condensation product obtained from ethidene chloride and benzene by

means of Al₂Cl₈ (p. 424) (see B. 21, 1176).

Substituted Anthracenes: Chlorine and bromine acting upon the CS₂-solution of anthracene first substitute the middle CH-groups with the production of y-mono- and dihalogen anthracenes. y-Dibrom-anthracene is also formed by the action of bromine

upon anthracene hydride (p. 424).

When anthracene is introduced into concentrated nitric acid, free from NO2, ms-Dinitroanthracene, C₆H₄(C. NO₂)₃C₆H₄, results. When this is carefully heated it sublimes without decomposition; if, on the contrary, it be rapidly heated, it decomposes readily into NO and anthraquinone: $C_6H_4(C.NO_3)_2C_6H_4 \longrightarrow 2NO + C_6H_4(CO)_2C_6H_4$. Fuming nitric acid and alcohol convert anthracene into anthracene ethyl nitrate, $C_6H_4 < \frac{CH(OC_3H_5)}{(NO_2)} > C_6H_4$, which also quickly charges to anthraquinone, but with

alcoholic potash yields pseudo-nitroso-anthrone, C₆H₄ C(OH) C₆H₄ (B. 24, R. 652,

947).

 β -Amido-anthracene, Anthramine, $C_8H_4(CH)_2C_8H_3$. NH₂, melting at 237°, and meso- or y-Amido-anthracene, decomposing at 115°, are produced on heating β -anthrol and anthranol (see below) with ammonia. meso-Diamidoanthracene, C₆H₄-(C. NH₂)₂C₆H₄, melting at 146°, results from the reduction of ms-dinitroanthracene.

Anthracene Sulphonic Acids result on treating anthracene with sulphuric acid and in the

reduction of anthraquinone sulphonic acids (p. 426). Anthracene carefully treated with

dilute sulphuric acid yields-

Anthracene Mono-sulphonic Acid, C₁₄H₉. SO₂H; its chloride melts at 122° (B. Concentrated sulphuric acid produces-

a- and \(\beta\)-Anthracene Disulphonic Acids, which form dioxyanthracenes on fusion with caustic potash.

(1) a- and β -Monoxy-anthracene, a- and β -Anthrol, behave like phenols or naphthols. β -Anthrol, from β -anthracene sulphonic acid and β -oxyanthraquinone, is changed by nitrous acid to α -Nitroso- β -anthrol, $C_6H_4(CH)_2C_6H_2(OII)(NO)$, which, upon reduction, yields α -Amido- β -anthrol. The latter may be oxidized to β -anthraquinone, C_6H_4 C_6H_5 C_6H_6 $C_$

with β-naphthoquinone. It corresponds to β-naphthoquinone (B. 27, 1438). It is only after the OH-group has been acetylated that the anthrols can be oxidized to oxyanthraquinones (see oxidation of phenols, p. 143).

Benz-Dioxyanthracenes: Two isomerides,-Chrysazol and Rufol,-having the formula $OH \cdot C_aH_a : (CH)_a : C_aH_aOH$, are obtained from a- and β -anthracene disulphonic acids. When their acetyl derivatives are oxidized and saponified, chrysasine and anthrarufin result. These are the corresponding dioxyanthraquinones (p. 426).

(2) ms Oxyanthracene, Anthranol, melting with decomposition at 165°, is prepared synthetically when concentrated sulphuric acid acts at 90° upon o-benzylbenzoic acid, C₆H₄ C₁C₁C₁C₆H₅ (p. 349) (B. 27, 2789). Zinc and acetic acid reduce anthraquinone to anthranol (along with dianthryl, (C₁₄H₉)₂ (B. 20, 1854). Anthranol can be readily oxidized to anthraquinone. Hydroxylamine hydrochloride converts it into anthraquinone oxime (B. 20, 613). For additional derivatives see B. 21, 1176; 28, R. 772.

Sunlight changes anthranol in benzene solution, similar to anthracene, into a diameter-

nel (B. 29, R. 1143).

ms Phenylanthranol, C_6H_4 $C_1(C_6H_5)$ C_6H_4 , melting at 141-144°, is formed when sulphuric acid acts upon triphenylmethane-o-carboxylic acid (compare p. 362). Its oxidation product is phenyloxanthranol. It yields phenylanthracene by reduction. Substituted triphenylmethane carboxylic acids form substituted phenylanthranols. In accord with their source, the hydroxyl phenylanthranols, like dioxyphenylanthranol, C_6H_4 $C_1(C_1H_4)$ $C_1(C$

Diphenylanthrone, $C_6H_4 < \frac{C(C_6H_6)_2}{CO} > C_6H_4$, melting at 192°, is a derivative of anthrone, $C_6H_4 < \frac{CH_2}{CO} > C_6H_4$, isomeric with anthronol. It is obtained by condensing unsymmetrical phthalylene tetrachloride (p. 240) with benzene, as well as from phenyloxanthronol by means of benzene and sulphuric acid (B. 28, R. 772).

Anthraquinone is reduced, when digested with zinc-dust and an alkaline hydroxide, to

ms-Anthrahydroquinone, C_6H_4 $C_6(OH)$ C_6H_4 . If exposed to the air it spin oxidizes to anthraquinone.

Dioxyanthranol, C_6H_4 , C_6H_4 , C_6H_4 , C_6H_4 , so-called anthrarobin, results when alizarin is reduced with zine dust and ammonia. It has been applied therapeutically in certain skin diseases.

Inthracene Carbevyli. Acids: The a- and β -acids, $C_6H_4(CH)_2C_6H_3COOH$, are formed from the anthracene-mono-sulphonic acids by means of the cyanides, and from the anthraquinone carbovylic acids by reduction with ammonia and zinc dust; the a-acid melts at 200°, the β -acid at 280°.

ms Anthracene Carboxylic Acid is formed from its chloride, which is produced when anthracene is heated with phosgene to 200° (B. 2, 678). It melts at 200° with decom-

position. Chromic acid oxidizes it to anthraquinone.

Hydroanthracenes.—Anthracene Dihydride, $C_{14}H_{12}$, results from the action of sodium amalgam upon the alcoholic solution of anthracene. It can also be obtained by many other synthetic methods. When heated with hydriodic acid and amorphous phorphorus to 220°, Anthracene hexahydride, $C_{14}H_{16}$, results. It melts at 63°, and boils at 290°. Anthracene perhydride, $C_{14}H_{24}$, is another product. It melts at 88° and boils at 270° (B. 21, 2510).

ms. Alkylic derivatives of anthracene dihydride are produced in the reduction of the alkyloxanthranols, and ms. dialkyl derivatives synthetically from alkylidene chlorides, benzene and Al₂Cl₈: ms. Dimethyl Anthracene Hydride, C₆H₆(CH · CH₂)₂C₆H₆, melting at 181°, yields anthraquinone by oxidation (A. 235, 305), just as benzophenone is ob-

tained from unsym. diphenylethane.

Anthraquinone or diketo-dihydroanthracene must be included with the derivatives of dihydroanthracene. Thereto belong also—

Hydro-anthranol and oxanthranol, which result in the reduction of anthraquinone with zinc-dust; and when acted upon with alkali and alkylogens, they yield alkyl derivatives :

$$\begin{array}{cccc} C_{6}H_{4} < & \stackrel{CH(OH)}{CH_{3}} > C_{6}H_{4} & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & \\ & & & \\ & & \\ & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & &$$

The alkylic hydranthranols, when boiled with hydrochloric acid, part with water and yield γ-alkyl anthracenes, which are also produced in the reduction of oxanthranols with zinc-dust. They are reduced by hydriodic acid to alkyldihydroanthracenes (B. 18, 2150; 24, R. 768; A. 212, 67).

Phenyl-oxanthranol results from the oxidation of phenylanthranol (p. 424). γ -Al-

kylic anthracenes are similarly oxidized to alkyloxanthranols.

Anthraquinone, Diphenylene diketone, C₆H₄(CO)₂C₆H₄, melting at 285° and boiling at 382°, sublimes in yellow needles. It is not only produced by the synthetic methods presented on p. 421, but also quite easily by the oxidation of anthracene with a chromic acid mixture (technical preparation, A. Suppl. 7, 285), as well as from anthra-hydride, ms-dichlor-, dibrom-, and dinitro-anthracene. It is, compared with the isomeric phenanthraquinone, very stable toward oxidants. It combines with hydroxylamine to anthraquinone-oxime, subliming above 200°. Sulphurous acid does not reduce it (unlike the true quinones).

It reverts to anthracene if heated to 150° with hydriodic acid, or with zinc-dust and ammonia. A variety of intermediate products are obtained in this reaction by simply applying different reducing agents:

$$\begin{array}{cccc} C_{e}H_{4} & CH(OH) & C_{e}H_{4} & C_{e}H_{4} & C_{C}(OH) & C_{e}H_{4} \\ \hline Oxanthranol & Anthrahydroquinone \\ C_{e}H_{4} & CH(OH) & C_{e}H_{4} & CH(OH) & C_{e}H_{4} \\ \hline C_{e}H_{4} & CH(OH) & C_{e}H_{4} & CHI_{2} & C_{e}H_{4} \\ \hline Anthranol & Hydranthranol. \end{array}$$

When fused with potassium hydroxide (at 250°), it decomposes into two molecules of benzoic acid; heated with soda-lime, it yields benzene and a little diphenyl.

Homologous Anthraquinones are obtained partly in the synthetic way and in part

by the oxidation of benz-alkylic anthracenes.

Methyl Anthraquinone, C₈H₄(CO)₂C₈H₃. CH₃, melting at 177°, from nitric acid and methyl anthracene, is also present in crude anthraquinone.

Substituted Anthraquinones: Monobrom-anthraquinone, melting at 187°, is formed in the oxidation of tribromanthracene. Tetrabrom-anthracene yields—

Dibrom-anthraquinone, which is also produced in the bromination of anthraqui-

none. It yields alizarin when heated with caustic potash.

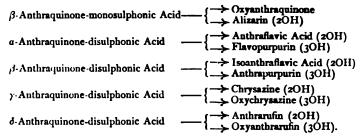
A mononitroquinone is obtained when anthraquinone is boiled with concentrated mitric acid. It melts at 230° (B. 16, 363).

Dinitroanthraquinone is formed on digesting anthracene with dilute nitric acid (I

eart with 3 parts water). It consists of yellow needles or leaflets, melting at 280°, and, like picric acid, manifests the property of forming crystalline combinations (Fritsche's reagent) with many hydrocarbons.

I-Amido-enthraquinone melts at 242° (B. 30, 1116).

When anthraquinone is heated with sulphuric acid, or when anthracene sulphonic are oxidized, various anthraquinone-mono- and di-sulphonic acids are prox When these are fused with caustic potash, mono- and poly-oxyanthraquinones are fo Some of these are valuable dyes:



The Oxyanthraquinones are derived (1) from the brom- and cl anthraquinones and from the sulphonic acids on fusion with alka when the substituting groups are replaced by hydroxyls.

By stronger fusion there generally ensues an additional entrance hydroxyl (oxy- and dioxyanthraquinones result from the mono-sulph acids); the same is true in the fusion of the oxyanthraquinones (B.

(2) The oxyanthraquinones may be synthetically prepared on hea phthalic anhydride with phenols (mono- and poly-valent) and sulph acid to 150°. The m-oxybenzoic acids (p. 421) also yield them w similarly treated.

The introduction of hydroxyl into anthraquinone and the oxyanthraquinones ca effected practically by persulphates in sulphuric acid solution. One or several hydr groups will then enter the anthraquinone molecule, depending upon the conditions w prevail (B. 29, R. 988).

Continued fusion with alkalies causes the oxyanthraquinones to separate into component oxybenzoic acids (same as anthraquinone decomposes into benzoic acid). this reaction aids in the determination of the position of the isomerides (B. 12, I:

A. 280, 1).

All anthraquinones are reduced to anthracene when heated with zinc-dust.

Individual hydroxyls in the oxyanthraquinones are reduced by heating the latter stannous chloride and sodium hydroxide (A. 183, 216). Heated to 150-200° ammonia water, single OH groups are replaced by amide groups.

(a) Moneyvanthraquinenes, $C_{14}H_1O_2(OII)$, the a- or Erythro-oxyanthraquine melting at 190°, and the β - at 323°, are formed simultaneously on heating toge phenol and phthalic anhydride. The β -body is also prepared from β -brom- or sulp anthraquinone.

Both oxyanthraquinones yield alizarin when fused with caustic potash.

(b) Dioxyanthraquinones: The members of this group contains two OH-groups in the 1,2-position (p. 422) are especially interesting, cause they unite with metallic oxides to form insoluble, very stable lak which adhere closely to the fiber. Their color varies with the chacter of the metal. They are, therefore, very valuable mordant d (B. 21, 435, 1164) (compare the similar behavior of the dioxyben; phenones, p. 348, of naphthazarine, p. 405, etc. For the theoretical si ALIZARIN. 427

consult B. 26, 1574). Alizarin, 1,2-dioxyanthraquinone, is the most important of these dyes.

Nine of the ten possible isomeric dioxyanthraquinones are known.

Alizarin, 1,2-Dioxyanthraquinone, melting at 290° and subliming at higher temperatures in orange-red needles, is the chief constituent of the dye of the madder root (Rubia tinctorium), in which it is contained as ruberythric acid (identical with morindin, from Morinda citrifolia).

Through the action of a ferment in the madder root, or when it is boiled with dilute acids or alkalies, ruberythric acid decomposes into glucose and alizarin:

Ruberythric acid $C_{26}H_{26}O_{14} + 2H_2O = 2C_6H_{12}O_6 + C_{14}H_6O_2(OH)_2$ Alizarin.

The alizarin products (garancin, etc.) obtained by such decompositions of madder root were formerly used in dyeing. At present they have been almost entirely supplanted by pure synthetic alizarin.

Artificial alizarin was first obtained by Graebe and Liebermann, in 1868, by heating dibrom-anthraquinone with potassium hydroxide. They had previously observed that the natural alizarin yielded anthracene when it was heated with zinc-dust. Alizarin is also produced from dichlor- and monobrom-anthraquinone, from the two oxyanthraquinones and anthraquinone sulphonic acid, by fusion with caustic potash.

Technically, it is made from anthraquinone prepared from purified (50 per cent.) anthracene. The latter is converted by fuming sulphuric acid into anthraquinone-monosulphonic acid, which is then fused under pressure for several days with caustic soda at a temperature ranging from 180-200°. Potassium chlorate is added as an oxidizing agent. The product of the reaction is sodium-alizarin, which is then decomposed with hydrochloric acid and brought into the market in the form of a paste (10-20 per cent.).

Alizarin also results, together with isomeric hystazarin, on heating

phthalic anhydride with pyrocatechin and sulphuric acid.

Alizarin dissolves readily in alcohol and other, and sparingly in hot water. It dissolves with a purple-red color in the alkalies; lime and barium salts throw out the corresponding salts as blue precipitates. Alums and tin salts produce red-colored precipitates (madder lakes); while ferric salts form blackish-violet and chromium salts violet-brown precipitates.

In cotton dyeing and printing the beautiful red lake and the almost black iron lake are generally employed. The goods are mordanted with alumina (by immersing them in aluminium-acetate, then heating, whereby aluminium hydroxide is deposited on the fibers) and then dipped into the solution of alizarin; the resulting alizarin-aluminate is fixed by the fibers. In dyeing with turkey-red it is customary to mordant the cloth with oil and alum, when the alumina then unites both with the oleic acid and with the alizarin.

Alizarin is decomposed by protracted fusion with caustic potash into benzoic and

protocatechuic acids.

B-Nitroalizarin, Alizarin Orange, C₆H₄(CO)₂C₆H(OH)₂(3)NO₃, consists of orangered leaflets, melting at 244°. It is produced by nitrating alizarin in glacial acetic acid or by the action of NO₂-vapors. It is prepared technically. Its alumina lake is orange in color. Alizarin-blue, a derivative of anthraquinoline (B. 18, 447), results upon heating it with glycerol and sulphuric acid (see Skraup's quinoline synthesis).

ing it with glycerol and sulphuric acid (see Skraup's quinoline synthesis). β -Amido-alisarin results by the reduction of β -nitroalizarin. Acetic anhydride converts it into an ethenyl compound, which proves that the amido-group occupies an

ortho position relatively to a hydroxyl group (B. 18, 1666).

Isomeric a nitro-alizarin (1,2,4) is obtained by the nitration of disceto-alizarin. It melts at 195° (compare B. 24, 1610).

Alizarin-amide, $C_{14}H_6O_2<\frac{NH_2}{OH^2}$, obtained by heating alizarin with ammonis-water to 200°, melts at 225°.

When nitro anthraquinones are reduced hydroxylamidoanthraquinones are formed;

these can be rearranged by sulphuric acid into amido oxyanthraquinones. Three of the dioxyanthraquinones isomeric with alizarin contain the OH-groups is one

benzene nucleus. They are:

(1,3) Purpuroxanthin, from phthalic anhydride and resorcinol; (1,4)-quinisaris, from hydroquinone; and, (2,3) hystazarin, from pyrocatechin (B. 28, 116). They are prepared more advantageously from their ethers, which result by the condensation of the corresponding dioxy-benzene ethers with phthalic anhydride and ALCla-

The following heteronuclear dioxyanthraquinones are produced when m-oxylenant

acid is heated:

(1.5) Anthrarufin, (1.7) Metadioxyanthraquinone, (2.6) Anthrafiavic Acid Isoanthrafiavic Acid is obtained from A-anthraquinone-sulphonic acid. Chrysan is another isomeride. It is obtained from its tetranitro-compound, $C_{11}H_{11}(N_{12}U_{12})$ (OH), the so-called chrysammic acid, by reduction and the replacement of the amid groups. This latter acid is obtained when aloes are digested with concentrate nitric acid. Consult B. 19, 2327, upon the spectra of the dioxyanthraquinones.

Homologous Dioxyanthraquinones: Dioxymethylanthraquinone, C11H3 (CH1)) (Oll), is chrysophanic or Rheinic Acid, melting at 178° (A. 284, 193). It exist in senna leaves (of the Cassia varieties) and in the root of rhubarb (from the Riese

variety). Zinc dust reduces it to methyl anthracene.

Chrysarobin, $C_{30}H_{36}O_{7}$, a reduction product of chrysophanic acid, occurs in gos-sne arrorol a powder. Air oxidizes its alkaline solution to chrysophanic acid. The same occurs in the animal organism (B. 21, 447).

Methyl-alizarin, melting at 250-252°, is isomeric with dioxymethylanthraquinee.

It is obtained from methyl anthraquinone sulphonic acid. It is very similar to a iras n

Various methylpurpuroxanthins have been prepared by the condensation of L55

droxybenzoic acid with o- and m toluic acids (B. 29, R. 141). Dimethyl-anthrarufin, $(CH_3)(OH)C_6H_2(CO)_2C_6H_2(CH_3)(OH)$, can also be obtained by the action of sulphuric acid upon sym. oxytoluic acid (B. 22, 3273).

(c) Trioxyanthraquinones.

These are produced on oxidizing anthraquinone disulphonic acids and dioxyanthraquinones, or upon fusing them with alkalies.

Purpurin, C_6H_4 C_{CO} $C_6H[1,2,4](OH)_3 + H_2O$, melting at 253° (anhydrous) and sublimable, is present with alizarin in the madder root. It is prepared artificially by heating alizarin and quinizarin with manganese dioxide and sulphuric acid to 150°. Is is also obtained from tribrom-It dissolves with a pure red color in hot water. anthraquinone. alcohol, ether, and the alkalies. Lime and baryta-water yield purple-ted precipitates. It yields a beautiful scarlet red with alumina mordants.

Purpurin amide, C14H5O2(OH)2NH2, is obtained on digesting purpurin with aqueous ammonia at 150°.

The following are isomerides of purpurin: anthragallol (1,2,3), a constituent of alizarin brown, anthra- or isopurpurin (1,2,7), and flavopurpurin (1,2,6), applied technically in dyeing and printing, and also oxychrysazin (1,2,5?). ('onsult A. 280. I, for the determination of the constitution of these bodies from the decompositions of the disulphonic acids genetically connected with them.

Homologous Trioxyanthraquinones: Emodin, and a trioxymethylanthraquinone, melting at 203° and isomeric with it, are formed, together with rhamnose, by the decomposition of frangulin, from the bark of Rhamnus frangula, by means of alcoholic

hydrochloric acid (B. 25, R. 371). Emodin also results from the decomposition of

(d) Tetra- and Poly-oxyanthraquinones: When oxyanthraquinones are heated with aming sulphuric acid, new hydroxyls enter these bodies, para-hydrogen atoms of the mon-substituted nucleus being replaced (J. pr. Ch. [2], 43, 231; 44, 103). Thus, elimin yields quinalizarin, alisarin bordeaux, C₁₄H₄O₂-1,2,5,8-(OH)₄.

Two tetraoxyanthraquinones, anthrachrysone and rufiopin, are obtained by heating symmetrical dioxybenzoic acid and opianic acid (p. 237) or protocatechuic acid (p.

227) with sulphuric acid.

Rufigallic Acid is a hexa-oxy-anthraquinone, C₁₄H₂O₂ - 1,2,3,5,6,7 - (OH)₈, which sformed when gallic acid is heated with sulphuric acid. It dissolves with an indigo**blue color** in alkalies.

It dyes chrom-mordanted material brown. It appears in trade in conjunction with anthrapurpurin as alizarin or anthracene brown. Anthracene blue, formed by the action of faming sulphuric acid upon dinitroanthraquinone, is an isomeric hexaoxyanthraquinone.

Anthraquinone Carboxylic Acids: a- and β -Anthraquinone Carboxylic Acids are produced in the oxidation of anthracene carboxylic acids. The a-acid (m. p. 285°) is also formed in the condensation of benzoyl phthalic acid and isophthalic acid (B. 29, **R.** 284), and the β -acid when chromic acid acts upon methylanthracene. The amide of the a-acid, treated with bromine and alkali, yields I-amidoanthraquinone (p. 425; B. 30, 2215). Trioxyanthraquinone Carboxylic Acid, purpurin carboxylic acid, C₁₄H₄. O₂(OH)₂CO₂H, is pseudo-purpurin, which occurs in crude purpurin (from madder). On heating, it decomposes into carbon dioxide and purpurin.

See C. 1894, 11, 784, for the synthetic purpurin carboxylic acids.

Naphanthracene, C₆H₄ C_H C₁₀H₆, melting at 141°, may be included among the homologous anthracenes. It is isomeric with chrysene (p. 416). It is formed when its quinone is digested with zinc-dust and ammonia.

Naphanthraquinone, $C_6H_4(CO)_2C_{10}H_6$, melting at 168°, is obtained from naphtoylo-o-benzoic acid, $C_6H_4<\frac{COOH}{CO...C_{10}H_7}$, the same as anthraquinone from benzoyl-benzoic

acid (B. 19, 2209; 29, 827).

GLYCOSIDES OR GLUCOSIDES AND PENTOSIDES.

Glycosides or glucosides are those vegetable substances which break down into sugars, chiefly grape sugar or glucose, and other bodies, when they are exposed to the action of unorganized ferments, enzymes (1, 587). Some of them decompose into isodulcite or rhamnose, a pentose, hence they are designated as pentosides. In many glycosides the exact nature of the sugar is not known. The glycosides and pentosides are therefore to be regarded as ethereal sugar derivatives. Some of them were described under their decomposition products, while many have been synthesized.

E. Fischer demonstrated that the simplest glucosides could be prepared by the action of hydrochloric acid upon alcoholic sugar solutions; they have been described (1, 549).

1. Myronic Acid, $C_{10}II_{10}NS_2O_{10}$, occurs as potassium salt in the seeds of black mustard. This crystallizes from water in bright needles. On boiling it with baryta-water, or by the action of the ferment myrosin, present in the seed, the salt decomposes into

glucus, allyl mustard oil, and primary potassium sulphate.

2. Arbutin, C₁₂H₁₆O₇, and Methyl Arbutin, C₁₃H₁₈O₇, are found in the leaves of Arbutus ava arsi. Arbutin crystallizes in fine needles, with ½-1 molecule of water,

and melts at 187° (B. 16, 800) in the anhydrous state. It is formed artificially from arbutin by the action of methyl io liv their decomposition we get, besides grape sugar, bydros

quinone:

 $C_{ts}H_{ts}O_{t}+H_{s}O=C_{s}H_{ts}O_{s}+C_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}H_{s}(O_{s}+O_{s}+O_{s}H_{s}(O_{s}+O_{s}+O_{s}H_{s}(O_{s}+O_{s}+O_{s}H_{s}(O_{s}+O_{s}+O_{s}+O_{s}+O_{s}+O_{s}+O_{s}+O_{s}+O_{s}+O_{s}+O_{s}+O_{$

3. Salicin, Ctall nO2, saligenin, glacers, melting at 1880 leaves of willows—c. g., Salix helix—and some poplars, from with water. It can be artificially prepared by reducing helic It forms shining crystals, which dissolve easily in hot water 1980. Its taste is bitter.

Oxidants convert it Into Actions, hence the saligenin in sali the phenol oxygen atom with the glucose. The enzymes My

decompose salicin into glucose and saligenin (p. 217) :

$$C_6H_{12}O_6$$
, O , C_6H_4 , CH_3 , $OH + H_3O = C_6H_{12}O_6 + HO$

Boiling dilute acids decompose it in a similar manner, but it changed to saliretin.

Populin, the benroyl derivative of salicin, C18H18(C7H3O)(hark and leaves of Populus tremula. It can also be artificial benzoic anliydride upon salicin.

Helicin, Salicylaldehyde-glucose, Call, (O. Call, Oa), CHO, salicin with nitric acid. It reverts to salicin upon reduction. pared from salicylic aldehyde and acetochlorbydrose. It is broi by ferments or dilute acids

Glucose-cumaraldehyde, $C_aH_{13}O_a \cdot O \cdot C_aH_4 \cdot CH = CH$ Methylgiuco o-cumar-ketone result from the condensation

and acetone (B. 24, 3180).

4. Amygdalin, Mandelo-nitrile diglucose, CmHmNO11+31

occurs in bitter almonds and in the kernels of Pomacese and A in cherries, peaches, apricots, and the leaves of the cherry laur lizes from alcohol in white, shining leaflets, and dissolves readily On boiling with dilute acids, or upon standing with water and em-in bitter almonds, amygdalin, is decomposed into oil of bitter hydrocyanic acid. When amygdalin is boiled with alkalies, th ammoonia, and amygdalic acid, Ca, H2, O13, is produced; this de acid and glucoses, when boiled with dilute acids.

Yeast separates but one molecule of glucose from amygdalin,

C.H. CH. CN O delnitrilo- or amygdonitriloglycoside, OCH.[CHOH] melting at 147-1490, which emulsin resolves into oil of bitter ali glucose (H. 28, 1508).

5. Coniferine, C18 H21O8 + 2H2O, is found in the cambium asparagus, and in the black root of Scoranera hispanica (B. 25, the air, and melts at 185°. It acquires a dark blue color when and hydrochloric acid. Boiling acids or emulsin decompose Coniferyl Alcohol, C₆H₂ (O. CH₃), C₅H₄. OH, which is oxidize

Glycovanillin, C₆H₃(O, CH₃)(O, C₆H₁₁O₅), CHO, the glue ing at 192°. Acids or emulsin split it up into glucoses and vanil Syringin, Methoxyl-coniferine, Cull 140 + H2O = C6H110 H.OH, occurs in the bark of Syringia vulgaris and Ligustrum 1910 and shows changes similar to those of coniferine.

6. Phloridzin, Cal HarO10, melting at 108°, occurs in the rou trees; hence the name, from plains, bark, and hisa, root. It is i pentosides: naringin and hesperidin. It breaks down into gra-

43I

the phloroglucin ester of p-oxyhydratropic acid, and the latter into phloroglucin (p. 165) and phloretic acid (p. 226):

$$\begin{array}{l} \textbf{C_{31}} \textbf{H_{34}} \textbf{O}_{10} + \textbf{H_{3}} \textbf{O} = \textbf{C_{6}} \textbf{H}_{12} \textbf{O}_{6} \text{ (Glucose)} \\ \textbf{C_{16}} \textbf{H}_{14} \textbf{O}_{6} + \textbf{H_{2}} \textbf{O} = \textbf{C_{6}} \textbf{H}_{6} \textbf{O}_{2} \text{ (Phloreglucin)} \\ + \textbf{C_{9}} \textbf{H}_{10} \textbf{O}_{3} \text{ (Phloretic Acid)}. \end{array}$$

7. Asculin, $C_{15}H_{16}O_9 + \frac{1}{2}H_2O$, melts at about 205° when it is anhydrous. found in the horse-chestnut, Asculus hippocastanum, and in the root of the wild jasmine, Gelsemium sempervirens. Acids or ferments resolve it into glucose and æsculetine

2. 4.5-dioxycoumarin. **3.** Daphnin, C₁₅H₁₆O₉ + 2H₂O, melting at 200°, is isomeric with the preceding. It is obtained from the bank of Daphne alpina. It breaks down into glucose and daph-

metin or 3,5-dioxycoumarin (p. 285).
 Fraxin, C₁₈H₁₈O₁₀, occurs in the bark of Fraxinus excelsior, and, like æsculin, in the bark of the horse-chestnut. It decomposes into glucose and fraxetin, the mono-

methyl ether of a trioxycoumarin (B. 27, R. 130).

10. Iridin, C₂₄H₂₈O₁₃, melting at 208°, occurs in the root of the violet, *Iris florentine*, etc. Dilute sulphuric acid resolves it into grape sugar and irigenin, C₁₈II₁₆O₈. The latter is probably a polyoxyketone. Concentrated caustic alkali decomposes it into formic acid, an aromatic oxyacid,—iridic acid, C₁₀H₁₂O₆, melting at 118°, which by loss of CO, becomes iridol or 3-oxy-4,5-dimethoxy-1-methylbenzene, melting at 57°, ad iretol, C, H,O4, or methoxyphloroglucin, melting at 186° (p. 165) (B. 26, 2010; 27,

R. 514).

11. Ruberythric Acid, $C_{14}H_{20}O_{14} = HO \cdot C_{14}H_{6}O_{2} \cdot O \cdot C_{12}H_{14}O_{3}(OH)_{7}$, melting at 258-260°, is the glucoside of alizarin (p. 427). It is formed in the madder root of hydrochloric acid into alizarin and glucose (B. 20, 2244). Purpurin is also contained in the madder root as a

glucoside.

12. Digitalin (Digitalinum verum, Kiliani), C29H46O12, is an amorphous glucoside. It is the active principle of the digitalis glucosides, which occur in the leaves of Digitalis urpurea and lutea. Concentrated hydrochloric acid breaks it down into digitaligenin, C₁₆H₁₅O₂, grape sugar, C₆H₁₅O₆, and digitalose, C₇H₁₄O₅.

Its therapeutic action consists in its occasioning "less frequent but more satisfactory

heart contractions."

The chief ingredient of the digitalis glycosides is without therapeutic action. It is crystalline digitonin, $C_{11}H_{44}O_{12}$, which is resolved by aqueous alcoholic hydrochloric acid into digitogenin, $C_{12}H_{44}O_{12}$, glucose, and galactose. The decomposition of the latter has led to a series of acids, the constitution of which is as yet undetermined (B. 27, R. 881; 28, R. 1056).

13. Saponin, $C_{10}H_{54}O_{18}$, from the root of Saponaria officinalis, is a white amorphous powder, which provokes sneezing and foams in aqueous solutions. Its decomposition yields glucose and sapogenin, $C_{14}H_{17}O_{2}$.

14. Convolvulin, C₃₁H₅₀O₁₆, from the jalapa root of Convolvulus purga, is a gummy mass, which is a powerful purgative. Among its decomposition products are, in addition to a sugar, d-Methyl-ethyl-acetic Acid, and an Oxypentadecylic Acid, CH₂CH₃CH₄(OH₃). CH₁₀C₉H₁₀. CO₂H, melting at 50°. Nitric acid oxidizes the latter to methyl-ethyl-acetic acid and an acid, C₁₀H₁₀O₄ (B. 27, R. 885), melting at 116°,

someric with sebacic acid (1, 455).

15. Jalapin, scammonin, C_MH₅₆O₁₆, from Convolvulus orizabensis, and from scammonium resin, yields acetic acid, tiglic acid, and palmitic acid upon distillation (B. 26,

R. 591; 27, R. 736).

16. Polygonin, C₁H₂₀O₅, melting at 203°, is a glycoside, and has been obtained from the root-bark of *Polygonum cuspidatum*. It yields emodin when it is decomposed with alcoholic hydrochloric acid (B. 29, R. 86).

Pentosides, Rhamnosides.—The following pentosides are to be regarded as ethereal compounds of rhamnose, $C_6H_{16}O_6 = C_6H_{12}O_5 + H_2O$ (1, 536), or of isodulcite:

Binz, "Grundzüge der Arzneimittellehre," p. 52.

1. Naringin, $C_{21}H_{20}O_{11} + 4H_2O$, melts when anhydrous at 170°. It is foul chiefly in the blossoms and also in other parts of the tree Citrus decumens of Jan. The name of the pentoside is derived from "naringi," a Sanscrit word meaning orage. Dilute acids decompose it into rhamnose and naringenin, melting at 230°. The later of the compose is the compose of the compose and naringenin, melting at 230°. is the phloroglucin ether of p-oxycinnamic acid, which concentrated caustic potash break down into phloroglucin (p. 165) and p-coumaric acid (p. 282) (B. 20, 296):

$$\begin{array}{c} C_{21} H_{12} O_{11} = C_{4} H_{14} O_{6} \ (Rhamnose) & + \ C_{15} H_{12} O_{5} \ (Naringenin) \\ C_{15} H_{12} O_{5} + H_{2} O = C_{6} H_{6} O_{3} \ (Phloroglucia) & + \ C_{7} H_{8} O_{3} \ (p-Coumaric Acid). \end{array}$$

2. Hesperidin, $C_{22}H_{26}O_{12}(?)$, or $C_{50}H_{60}O_{22}(?)$, melting at 251°, is present in unity oranges, lemons, etc. It decomposes, when heated, into glucose, rhamnose, and hesperetin, melting at 226°. Caustic potash resolves the latter into phloroglucia and isoferulic acid (p. 283) (B. 14, 948):

$$\begin{array}{ll} C_{50}H_{50}O_{27}+3H_{2}O=2C_{6}H_{12}O_{6}+C_{6}H_{14}O_{6} \ (Rhamnose)+2C_{16}H_{14}O_{6} \ (Hesperein) \\ C_{16}H_{14}O_{6}+H_{2}O=C_{6}H_{6}O_{3} \ (Phloroglucin)+C_{10}H_{16}O_{6} \ (Isoferulic Acid). \end{array}$$

3. Quercitrin, C₂₁H₂₂O₁₂, is present in the bark of *Quercus tinctoria* and is applied under the name quercitrone as a yellow dye. It breaks down into rhamnose and quercetin (see this), a phenylbenzopyrene derivative (B. 26, R. 234; 28, 2303):

$$C_{21}H_{22}O_{12} + H_{2}O = C_{6}H_{14}O_{6}$$
 (Rhamnose) + $C_{15}H_{60}O_{7}$ (Quercetrin).

4. Frangulin, C₁₁H₂₀O₂, melting at 286°, occurs in the bark of *Rhamnus français*. When it is saponified with alcoholic hydrochloric acid rhamnose, *emedin* (p. 429) and a trioxymethylanthraquinone, isomeric with the latter, are produced (B. 25, R. 370):

$$C_{21}H_{20}O_{97} = 2H_2O = C_6H_{16}O_6 \text{ (Rhamnose)} + C_{15}H_{10}O_5 \text{ (Emodin)}.$$

BITTER PRINCIPLES.

Under the head of "bitter principles," or indifferent substances, is embraced a class of vegetable bodies many of which have already found their place in the chemical system. Those yet uninvestigated are:

Aloin, $C_{17}H_{18}O_7$, or $C_{17}H_{16}O_7$ (?) (B. 23, R. 207), found in aloes, the dried sap of many plants of the aloe variety. It forms fine needles, possesses a very bitter taste, and acts as a strong purgative. If digested with nitric acid it yields abortic acid, $C_{14}H_4(NO_1)C_1$ (RCC) (CO). (NO₂)₄(OH)₂. Anthracene is formed when aloin is heated with zinc-dust (B. 1, 105) It forms aloreinic acid, $C_9H_{10}O_3+H_2O_5$, when fused with caustic potash. down into orcin and acetic acid.

Cantharidin, $C_{10}H_{12}O_4$, melts at 218° and sublimes readily. It is contained in Spanish flies and other unsects. It tastes very bitter and produces blisters on the skin it dissolves and other unsects. It is contained in spanish flies and other insects. It tastes very bitter and produces Disters on the same lit dissolves when heated with alkalies and forms salts of cantharinic acid, $C_{10}H_{11}O_{2}$ it combines with phenylhydrazine to an addition product, $C_{10}H_{20}N_{2}OH$, melting at 194°, and a phenylhydrazone, melting at 238° (B. 25, 140). Hydriodic acid converts cantharidin into cantharic acid, $C_{10}H_{12}O_{4} = C_{8}H_{11}O$. CO. CO₂H₄ isomeric with it. When this acid is distilled with lime, cantharene or dihydro-o-xylene (p. 294) results.

Picrotoxin, $C_{15}H_{18}O_6 + H_2O_7$, is found in the grains of cockle, and crystallizes in fine digested with hydriodic acid it becomes picrotoxic acid, $C_{15}H_{18}O_4$ (B. 24, R. 912), and the grains of cockle is a series of cockle in the grains of cockle in the grain in

melting at 134°. Santonin, $C_{15}H_{10}O_{3}$, melting at 170°, $[a]_{\rm n}=-171.37^{\circ}$, is the active principle of down at 120° into water and santonin. On boiling with baryta-water we have formed salts of isomeric santonic acid. $C_{15}H_{20}O_{4}$, which breaks salts of isomeric santonic acid. $C_{15}H_{20}O_{4}$, which breaks salts of isomeric santonic acid. $C_{15}H_{20}O_{4}$, which melts at 171°. salts of isomeric santoic acid, $C_{15}H_{20}O_4$, which melts at 171°.

This acid, upon further oxidation, yields a tetracarboxylic acid. For its constitution see B. 29, R. 1119. Santonin is a lactone. It bears the same relation to santonic and santoic acids as coumarin to coumarinic and countaric acids. Again, it contains the ketone group; its phenylhydrazone melts at 220°. When santonin is reduced with hydriodic acid or with stannous chloride and hydrochloric acid, santous acid, C₁₆H₂₀O₃, results. This is dextro-rotatory and melts at 179°. The corresponding laworotatory modification and the (d + 1)-acid are known. When these three acids are fused with caustic potash, propionic acid, dimethyl-\(\beta\)-aphthol, and hydrogen are produced. Hence it would seem that santonin is a derivative of a hexahydrodimethylnaphthalene (B. 27, 530; 28, R. 392; 29, R. 291, 296). When santonin is reduced with tin and hydrocarbon acid, not only santous acid is formed, but also a hydrocarbon, C₁₀H₁₅(CH₂)₂(C-H₂), boiling at 248°, which probably is dimethylethyloctohydronaphthalene (B. 28, R. 622).

The conversion of santonin in acetic acid solution, in sunlight, into photosantoic acid, C₁₈H₂₂O₅, and in alcoholic solution into photosantoic ethyl ether (B. 18, 2859),

s remarkable.

NATURAL DYES.

The important natural dyes, indigo, alizarin, and its allies, euxanthic acid, gentisin, etc., have found their place in the system of organic chemistry. The following are some of the natural dyes which have not yet been investigated:

Brasilin, $C_{16}H_{14}O_{5}$, is found in Brazil-wood and red-wood; crystallizes with $1\frac{1}{2}H_{2}O$ in white, shining needles, and dissolves in alkalies with a carmine-red color on exposure to the air. Acids then precipitate *brasileīn*, $C_{16}H_{12}O_{5}+H_{2}O$, from the solution. The action of iodine upon brasilin also produces this compound. It regenerates brasilin by reduction. When distilled, it yields resorcinol.

Brasilin forms mono-, di-, tri-, and tetra-alkyl ethers (B. 27, 524; R. 304; 29, R.

219)

Hematoxylin, $C_{16}H_{11}O_6 + 3H_2O$, the coloring-matter of logwood (Hamatoxylon Camberkianum), is very soluble in water and alcohol, and crystallizes in yellowish prisms having a sweet taste. It dissolves in alkalies with a violet-blue color. When distilled or fused with potassium hydroxide, pyrogallic acid and resorcinol result from it. If the ammonium hydroxide solution be allowed to stand exposed to the air, there results harmatein-ammonia, $C_{16}H_{11}(NII_4)O_6$, from which acetic acid precipitates the free harmatin, $C_{16}H_{11}O_6$ (at 120°), a reddish-brown body, which has metallic lustre after drying (A. 216, 236). It yields penta-ethyl- and penta-acetyl ethers. The behavior of brasilin and harmatoxylin seems to point to relations between these two bodies and the xanthone and fluorane derivatives (B. 22, R. 558; 27, R. 304; 29, R. 219).

Carthamin, $C_{14}H_{16}O_{7}$, occurs in safflower, the blossoms of Carthamus tinctorium, and is precipitated from its soda solution by acetic acid as a dark red powder, which, on drying, acquires a metallic lustre. It dissolves with a beautiful red color in alcohol and the alkalies. It yields para-oxybenzoic acid with caustic potash (A. 136,

117).

Curcumin, $C_{14}H_{14}O_4$, the coloring-matter of turmeric root, from *Curcuma longa* and *visridiflora*, crystallizes in orange-yellow prisms, melts at 177°, and dissolves in the alkalies to brownish-red salts. Ethyl vanillic acid is obtained on oxidizing diethyl-curcumin with potassium permanganate (B. 17, R. 332).

Luteolin, Maclurin, see p. 228.

Litmus, see p. 162.

Usninic Acid, Lichen Substances, etc.—A. 295, 222; B. 30, 357.

Carminic Acid, $C_{11}H_{11}O_{1}$, is found in cochineal, from Coccus cachi coccinelliferi, an issect peculiar to different cactus varieties. It is a purple-red mass, dissolving readily in water and alcohol, which forms red salts with the alkalies. Boiling nitric acid converts into mitrococcic acid (p. 226). Bromine converts carminic acid into two bromides, a tribromide (β) and a tetrabromide (a), which by further decomposition yield methyl-

434

dibromasyphthalic acid, HO[4]C₀[3,5]Re [6]CH₀[1,2](CO₀H)₀. The β-bromi probably an a-napthoquinone derivative, and carminic acid the hydrate of a methylic anaphthoquinone (p. 405) (R. 26, 2647; 27, 2989).

Potassium persulphate exidises the cochineal dye to two acids, which can be sepa by their varying solubility in water. They are cachenillic acid and caccinic Bromine converts the first into tribromareaotinic acid (B. 30, 690). Cochine applied in wool-dyeing for the production of scarlet-red colors. This application diminished very greatly since the discovery of the red annother. His Rederick restricts diminished very greatly since the discovery of the red aso-dyes, like Bieberick scarle others.

Chlorophyl, Leaf Green, occurs in all the green parts of plants and in the ch phyl granules, which also contain wax and other substances. The composition of ch phyl has not yet been established. There appears to be some iron in it. See A. 81, for the decomposition of chlorophyl with alkalies and acids. It is rather remark that chlorophyl substances yield pyrrol when they are distilled with sinc-dust, hence: appear to be intimately related to this substance. This observation was also made the blood substances (I, 585). The hamatoporphyrin obtained from the latter sh great similarity in absorption spectra to the phylloporphyrin from chlorophyl, so there seems to be some connection in the constitution of blood and vegetable dyes (B. 29, 1766; R. 415).

III. HETEROCYCLIC COMPOUNDS.

The carbocyclic substances treated in the preceding section belong to the class of isocyclic compounds which consist of rings of atoms of one and the same element. Apparently, very few elements are adapted to such a ring-formation.*

However, substances are known in great number and complexity which are based upon ring-skeletons consisting of atoms of various elements. These bodies have been arranged under the designation "heterocyclic compounds." It is true that a series of inorganic bodies † can be included in this category, but it is our purpose to consider only the "organoinorganic"—i. e., those ring-systems the members of which are formed from carbon in union with other elements, most important of which are oxygen, sulphur, but especially nitrogen. In many cases sulphur can be replaced by selenium, and there are some substances known in which phosphorus forms a ring with C-atoms. †

From the standpoint of organic chemistry, the basal element of these rings is carbon, and accordingly the members not produced by C-atoms are designated as *hetero-atoms*, and distinguished as *mono-*, *di-*, *tri-*, *tetra-*, etc., hetero-atomic rings, depending upon whether one, two, three, four, or more hetero-atoms have participated in their formation. To express the number of atoms constituting the entire ring, the rings are termed

three, four, five, six, and poly-membered rings.

Many heterocyclic compounds have been discussed in the preceding chapters—for example, the cyclic ethers of the glycols and thioglycols, like ethylene oxide, diethylene dioxide, diethylene disulphide; the cyclic alkylenimides, like tetramethyleneimide or pyrrolidine, diethylenediimide, or piperazine; the cyclic esters of oxy- and amido-acids, like the lactides, the lactones, the lactams; the cyclic derivatives of dibasic carboxylic acids, like anhydrides, imides, alkylen esters, alkylenamides, etc. (see 1, 313; ring-shaped compounds). These bodies attached themselves, as their names indicate, naturally to known classes of compounds with open chains. They can be readily obtained from substances with open chains and be equally readily changed back into them. In the succeeding sections, however, a series of heterocyclic bodies will be described which manifest

^{*} Nitrogen, mainly, in addition to carbon. The allotropic modifications of many elements are probably induced by the formation of isocyclic rings— $\epsilon.g.$, that of oxygen in ozone, O_g , and that of sulphur in the molecular weight, S_g , etc.

[†] See Bischoff, "Handbuch der Stereochemie," p. 641.

[‡] Finally, rings are present in the salts of dicarboxylic acids, sulphocarbonic acids, disulphonic acids, glycols, etc., containing bi- and polyvalent metals. Members are formed by the metal atoms.

varying deportment in so far that the rings upon which they are constructed can not be resolved in a simple way. Such rings are rather nuclei to which derivatives attach themselves which are related to the fundamental substances, the same as the aromatic substances are related to benzene. Usually, these substances, like benzene, contain unsaturated unions.

It has, therefore, been assumed that in these rings, as in benzene, there is a particular the stability of these bodies. If the potential valences are dissolved by the addition of hydrogen or some such substance, then saturated bodies result; these posess the dicyclic character (see p. 18), and so far as their decomposability is concerned, bey in the main exhibit the character of the heterocyclic substances discussed after the futy losdies. A real fundamental difference, however, between the two rings just described does not exist. Compounds were studied in connection with the lactones and dibest anhydrides which offered great resistance to decomposition by water absorption, or (see 1, 379 462, 465). On the other hand, there are many bodies in which potential linkages are assumed which are very easily decomposed by certain reagents - e.g., pynol by hydroxylamine yielding succinaldehyde-dioxime (1, 327), and glyoxaline by beauth chloride and sodium, forming dibenzoyldiamidoethylene, etc.

The heterocyclic rings containing five and six members are, like the analogous carbon rings, the most stable and important. They will be treated in this section. The tendency to the formation of six-membered rings is shown also in the processes of polymerization; formaldehyde, by the coalition of three molecules, becomes six-membered trioxymethylene: acetaldehyde becomes the six-membered paraldehyde, and the cyanogen compounds polymerize to derivatives of a six-membered ring, consisting of 3 C- and 3 N-atoms, etc. (compare also the aromatic polymerization Three- and four-membered rings are usually formed with extreme difficulty, and are easily torn asunder (p. 443). The seven-ment bered rings are not well known, and are also unstable (B. 27, 2902: 28, R. 756). Special mention may be made of substances like diphenic anhydride and diphenimide, which contain seven-membered rings (p. 341). Individual compounds are known in which heterocyclic rings are assumed to be present which contain eight or more members.

Eight-membered rings are present in the conditional phenyl and benzil (B. 26, 1704): $C_6H_5C=N-C_6H_4$, melting at 238°. Upon reduction this yields a tetrahydro derivative, a base, melting at 154°. Diphenhomazine (p. 347), $C_6H_4 < N^{-2}C(C_6H_6) = N > C_6H_4$, results from the conditional phenomena and finally, the cyclic alkylon Eight-membered rings are present in the condensation product of og-diamidodi-

densation of two molecules of o amidobenzophenone; and, finally, the cyclic alkylen esters of the succinic acid series (A. 280, 169); compare-

CO-NH-NH-CO Hydrazioxalyl, co-NII-NH-CO It is probable that (B. 29, R. 180). a 13-membered ring is present in cycloformazyl formic ester,

CO₂R · C N · NH[4]C₆H₄ (p. 339), and a sixteen-membered ring in tetrasalicylide $N: N[4]C_6H_4$ (p. 225).

Consideration in the sense of A. v. Baeyer's strain theory (p. 19) is rendered difficult

E

by the varying nature of the hetero-atoms entering into the composition of the ring.

Certain facts most certainly contribute to the representation of the spacial relations of recommendation. Thiophene, with a ring of four CH-groups and one S-atom, greatly resembles benzene, containing six CH-groups. Thiazole, consisting of three CH-groups, one N-atom, and one S-atom, similarly resembles pyridine, which has five CH-groups and one N-atom. It would therefore seem that a sulphur atom is capable of replacing the bivalent group —CH — CH— in the ring:

It is an almost universal rule that an N-atom can replace a methine group in a ring without causing any essential loosening of the ring-union. If we suppose a methine group in benzene to be replaced by N, the product will be pyridine, which is about as stable a ring as we have in benzene. And if the methine groups in pyrrol be successively replaced by one, two, and three N-atoms, there also results a series of derivatives in which ring-stability is very evident:

A general review of the many heterocyclic ring systems can be obtained from two points of view. *Homologous series* are obtained by arranging together the rings with similar hetero-atoms according to the increasing number of C-members. The following series of rings have been deduced in this way:

(a) WITH AN O-MEMBER.

:cc:	:c_c;	: ccc:	: c—c—c—c:
H ₂ C—CH ₂ O Ethylene Oxide	H ₂ C-CH ₂ -CH ₂ O Trimethylene Oxide	H ₂ C—CH ₂ —CH ₃ —CH ₃ Tetramethylene Oxide	H ₂ C-CH ₂ -CH ₂ -CH ₃ -CH ₃ Pentamethylene Oxide
_	_	H ₂ C—CH ₂ —CH ₂ —CO Butyrolactone	H ₂ C-CH ₂ -CH ₂ -CH ₃ -CO Valerolactone
-	_	OC—CH ₂ —CH ₂ —CO O Succinic Anhydride	OC—CH ₂ —CH ₂ —CH ₂ —CO Glutaric Anhydride
-	-	HC = CH - CH = CH Furfurane	HC = CH—CO—CH = CH Pyrone

(b) WITH AN S-MEMBER.

		· · · · · · · · · · · · · · · · · · ·	
:c <u></u> c:	: c—c:	:0-0-0-0:	: <u></u>
н,с-сн,	н,с-сн,-сн,	COOH . CH—CH ₃ —CH ₃ —CH . COOH	_
[Ethylene Sulphide]	[Trimethylene Sulphide]	Tetrahydrothiophene-dicarboxylic	
	_	CO—CH _g —CH _g —CO Sulphosuccinyl	-
_	_		CH=CH-CH ₂ -C(CH) ₃ =
		Thiophene	Methylpenthiophene

(c) WITH AN N-MEMBER.

: CC:	:c—c:	: cċċc:	: c—ë—ë—ë—c:
CH ₂ —CH ₂ NH [Ethylenelmide]	CH ₂ —CH ₂ —CH ₂ NH Trimethyleneimide	CH ₂ —CH ₂ —CH ₂ —CH ₂ NH Tetramethyleneimide Pyrrolidine	CH ₂ —CH ₂ —CH ₂ —CH ₃ —CH NH———————————————————————————————————
-	-	CH ₂ —CH ₂ —CH ₂ —CO NH Butyrolactam	CH ₂ —CH ₂ —CH ₂ —CO NH—Valerolactam
OC — CO NH∕ Oxalimide	_	OC—CH ₂ —CH ₂ —CO NH Succinimide	OC—CH ₂ —CH ₂ —CH ₂ —CO NH— Glutarimide
_	_	CH = CH—CH = CH NH Pyrrol	CH—CH = CH—CH = CH N—Pyridine

Complication by virtue of isomerides arises in the case of rings having two hetero-atoms. These isomerides are occasioned by the varying positions of the hetero-atoms with reference to one another—e. g.:*

^{*}In the following paragraphs the individual ring-types are represented in diagram to save space. The valences remaining free in the case of the different atoms after the ring-formation are indicated by dots, and the most important compounds or classes of regards are arranged under the various rubrics to which they belong.

RINGS WITH TWO N-MEMBERS.

: C N. N. N. Hydrazi Compounds, Diazomethane	: C—N . ; : C—N . Dimethylaziethane	: C—N . : C—N . C—N . Pyrazole Group	: C—C—N . : C—C—N . :: Pyridazine Group
_	. N—C: : C—N. Ethidene Urea, Dicyan-compounds	: C C N . I I N — C : Glyoxaline Group, Cyclic Ureas	: C—N—C: : C—C—N: Pyrimidine Group, Cyclic Ureas
_	-	-	: C—N—C: : C—N—C: Pyrazine Group Diethylene-diimide

RINGS WITH AN O- AND AN N-MEMBER.

: C O N P-Benzaldoxime Ether	: C—O 	: c CON CON Isoxazole Group	: C—C—O : C—C—N . Orthoxazine Group
-	-	COC:	: C—O—C: : C—C—N. Metoxazine Group, Pentoxazoline
_	_	_	C—O—C C—N—C Paroxazine Group

The three- and four-membered systems naturally disappear in the series of rings having three and four hetero-atoms. The branching of the series in consequence of position-isomerides with the hetero-atoms becomes more frequent, so that the relations dependent upon homology frequently become obscure. In the monohetero-atomic rings also the homology usually appears solely in the case of the saturated (alicyclic) ring-systems, whereas the more important unsaturated systems, with more pronounced aromatic character, show at times very varying deportment—

ORGANIC CHEMISTRY.

e.g., memu pyridia. great difere. ologous series with an N-member the group of the fivenes into juxtaposition with that of the six-memberd he representatives of these two groups manifest very heir behavior.

Hence it is more practical to group the ring systems according to the number of members composing the ring. In this manner only system of rings of approximately like stability will come together, and they will therefore, very probably yield similar derivatives. Hence to groups of three rings will be attached such as have four, five, six, etc., members. Each of these groups will have subdivisions in accordance with the number of hetero-atoms, so that, for example, in the group of five-membered heterocyclic rings there will be discussed first the monohetero-atomic, then the di-, tri-, and tetrahetero-atomic systems. This might be called grouping according to isologous series:

THREE-MEMBERED HETEROCYCLIC SUBSTANCES.

: C—C:	Ethylene Sulphide	CCC:
C-N. B-Benraldorime Ether	: C—N. S Thialdolaniline (p. 79)	C—8.

FOUR-MEMBERED HETEROCYCLIC SUBSTANCES.

-	: C—N—C :CAlkylidene-#-thioureas	: C—N—C: N/ Alkylidene Ureas, Dicyanogen Compounds (?)
CCN. Betaine	: c—c—o	Dimethylaziethane
Trimethylene Oxide	:c-c-e: \s'	Trimethyleneimide



FIVE-MEMBERED HETEROCYCLIC SUBSTANCES.

HETEROCYCLIC COMPOUNDS.

Purfurane, 7-Lactones, Succinic Anhydride	: C—C—C : S Thiophene, Sulphosuccinyl	: C—C—C : See Selenophene	: C—C—C: N Pyrrol, y-Lactams, Succinimide
: C—C—C—N .	: C—C—C—N .	_	: C—C—C—N. N Pyrazole Group
Cyclic Ethers and Esters of Glycol, Aldehyde, Carbonic Acid, and Oxalic Acid	: C—C—S—C: S—C: Ethidene - ethylene Disulphide	-	: C—C—N—C:
: C—C—N—C: Oxasole Group	: C—C—N—C:	: C—C—N—C: Se—Selenazole Group	Glyoxatine Group, Cyclic Ureas
: C—C—N—N Diazo-oxides	: C—C—N—N S Diazosulphides	: C—C—N—N Se—————————————————————————————————	: C—C—N—N N Osotriazole Group, Azimides
. N—C—C—N. Furazane Group	. N—C—C—N . S Piazthioles	. N—C—C—N . Se Piaselenoles	
C-N-C-N. Azoximes	: C—N—C—N .	_	: C—N—N—C : N Triasole Group
: C—N—N—C: Oxybiazole Group	: C-N-N-C: S Thiobiazole Group		
- .	. N—C—N—N .	_	: C—N—N—N . Tetrazole Group
			



Pentamothylene Outde, 8-Lactores, Gletaric Acid An- hydride. Pyrone Group.	Parthiphar Group	Postant de la
Carbenyl-onime Anhydrides 1 C C C C C C C Cyclic Ethers and Enters of Trimethylene Glycol Aklehyde, Carbonic Acid, and Carbon	10-0-0-6-C: Totressethylene Disalphides	.0-0-0-0-
Pentox a reline Group ; C—C—C—C : Diethylene Oxide, Cyclic Anhy-	Penthiaseline Group : C C 8 C C t Diethylene Disulphide	وسنسبرم
Paroxasine Group : C—C—S—C—C: O Thio-diglycollic Anhydride	: C—C—N—C—C: Perathiasine Group	Pyrasiie G
Azoxazine Derivatives : C—N—C—C—N. O Benzenylamidoxime Acetic Anhydride : C—O—C—O—C: Polymeric Aldehyde	: C—C—N—N . Diarthine Derivatives : C—S—C—S—C: Trithioaldehyde	N-C-C- N- Osotriazine I : C-N-C- N- UnsymTria : C-N-C- N Polymeric Cyanog Cyanidina
O—N—C—C—N. O Glyoxime-hyperoxide	· _	Osoletrasones, C—N—N Tetrasin

indene, naphthalene, anthracene, etc., are derived from benumerous di- and polycyclic, condensed nuclei are obtained from cyclic rings that contain adjacent C-members. This is possible t that the two adjacent C-members participate also in the formaromatic rings, like benzene, naphthalene, phenanthrene, etc. idensed nuclei unite, as a rule, the properties of the carbocyclic e of the heterocyclic ring. When definite names are not hem, as in the indol and quinoline groups, they are designated prefixes benzo- or phen-, dibenzo- or diphen-, naphtho-, etc., name of the heterocyclic ring.

quently substances having such condensed nuclei have the heterocyclic ring dare then changed to ortho-substitution products of the carbon ring. Again, clic ring shows itself more stable toward oxidizing agents, so that it is possins of potassium permanganate, etc., to oxidize the condensed nuclei with of the carbon ring and the production of ortho-dicarboxylic acids of the rings. Thus, acridine yields quinoline dicarboxylic acid, quinoline a pyrioxylic acid, benzoglyoxaline a glyoxaline-dicarboxylic acid, benzotriazole a urboxylic acid, and phenazone a pyridine tetracarboxylic acid, etc.

e simple and condensed heterocyclic compounds have, as a rule, le by the inner condensation of suitable fatty or fatty-aromatic ving open chains. Very often the intermediate products, leadly to the ring, cannot be fixed because of their great inclination 5-formation; orthosubstitution products of benzene and naphtha-38, 390) are especially well adapted for the production of conterocyclic nuclei. They have afforded the starting-out material eparation of an immense number of substances belonging in this

eterocyclic bodies also occur in technical and natural products. and important family of vegetable alkaloids belongs in the pyridine and the hydropyridines. Pyridines and pyrrols occur rand bone-tar. Thiophene and coumarone are also present in Furfurol and other derivatives of furfurane have been found from wood. The important vegetable dye, indigo, and its lies, are derivatives of indol. Many heterocyclic bodies prethetically have been manufactured upon a technical scale, beheir coloring and therapeutic properties. This is true of the paroxazine, parathiazine, and paradiazine-series, e.g., resorufin, blue, toluylene red, safranine, etc.; the dyes of the thiazole-group, of the important febrifuges, like antipyrine, salipyrine, tolypyrine, to the pyrazole-group, and piperazine or hexa-hydropyrazine,

npare Kühling, "Stickstoffhaltige Orthocondensationsproducte," 1893.

1. THREE-MEMBERED HETEROCYCLIC COMPOUNDS.

As a rule, bodies of this class manifest "ring-strain" to a greate gree than the carbocyclic substances of the trimethylene series. The they are inclined, in consequence of a rupture of the ring, to tan additional atoms or atom groups. Hence, they are produced only the most favorable conditions, and many compounds which formerly regarded as based upon three-membered heterocyclic rings have, as sult of more recent study and investigation, had their formulas down or have been discovered to be still higher steps in polymerization; pare ethyleneimide, glycolide, etc.

A. MONOHETEROATOMIC THREE-MEMBERED RINGS.

- (a) Having an O-member: Ethylene Oxide, H_3C O. The method of preparation of the aliphatic series (1, 298). It exhibits a great inclination toward a rupture ring. This is shown by the fact that it precipitates the hydroxides from solutions metals with the simultaneous formation of glycolacidylhydrins. The same tende observed with the substituted ethylene oxides, like tetramethylethylene oxide (1, 290 glycide derivatives (1, 476; 11, 256), condensed nuclei containing the ring of ethoxide—e. g., tetrahydronaphthylene oxide (p. 413) and diketotetrahydronaphtoxide (p. 413), etc.
- (b) Having an S-member: Ethylene Sulphide, H_1^{C} S, corresponding to eth oxide, is apparently not capable of existing. It is usually its polymerides white obtained: $(C_1H_4S)x$ and $(C_2H_4S)_2$ diethylene disulphide (1, 305); compare in Sulphide, C_6H_6C S (p. 375). See also the addition products of sulphur with eth and acetylene derivatives—B. 28, 1635; 30, 110.
- (c) Having an N-member: Ethylene Imide, H₂C NH, also appears unstable. I ene diamine hydrochloride and others rather yield the six-membered ring of pipe (1, 314). It is assumed that oxalimide, CO NH (1, 436), as well as the lactimides,—benzoyl-amido-cinnamic acid lactimide, Co NCOC₆H₅ (p. 276),—con three-membered ring consisting of two C-atoms and one N-atom.

B. DIHETEROATOMIC THREE-MEMBERED RINGS.

Rings, consisting of C, N, and O, are assumed to be present in the nitrogen ether some of the aldoximes—e. g., the n-alkyl benzaldoximes, RN O (p. which are resolved by acids into benzaldehyde and n-alkylhydroxylamines. The

ring occurs in different polycyclic substances,— ϵ . g., the isatogen compounds,—such as isatogenic acid, C_0H_4 (p. 284), and in the products obtained by reduc-

ing acidylated o-nitranilines with ammonium sulphide—e. g., C₆H₄ NH—CCH₃ (see benzimide azole), etc. Compare also anthranil and anthroxan aldehydes (pp. 211, 250). Thialdolaniline, C₆H₅N—CH—CH(OH). CH₃, contains a ring consisting of C, N,

and S. The same may be observed of similarly formed compounds (see Usèbe's green,

p. 359).

Hydrazi- and Azimethylene-group: Substances consisting of two N- and one C-atom are much better known. The hydrazi-derivatives belong in this class. They are obtained from the hypothetical hydrazimethylene, NH>CH₂ (Curtius, J. pr. Ch. [2], 44, 169, 554). They are produced in the action of hydrazine upon o-diketones and a-ketone carboxylic esters (1, 328)—e. g., benzil, diacetyl, pyroracemic ester:

Benzoylphenylhydrazimethylene, C_8H_8 . CO. $C(C_8H_8) < NH \over NH$, melts with decomposition at 151°, and diphenyldihydrazimethylene,

Hydraziacetic Acid, HN CH . COOH (1, 366), and Hydrazi-propionic Methyl

Reter, HN C(CH₃). COOCH₃, melting at 82°. The potassium salt of a sulpho-

hydraziacetic ester, $\frac{HN}{KO_2SN}$ CH . $CO_2C_2H_5$, has been made by the action of potassium sulphite upon diazoacetic ester (B. 28, 1848).

The hydrazi-compounds are readily changed by oxidation to the azi-derivatives containing two atoms less of hydrogen. They evolve nitrogen on the application of heat.

See 1. c. for other rearrangements. Benzhydrazoln, CaH₅N CII . Call₅ (p. 185), formed from benzaldebyde and hydrazobenzene, is a triphenyl hydrazimethylene.

The diazo-compounds of the aliphatic series are obtained from azimethylene or diazomethane. The latter is produced when nitrosomethylurethane is digested with methyl alcoholic potash. Compare vol. 1, 206, for its properties. It also results from the reduction of methyl nitramine (1, 171; B. 29, 961), and from the action of hydroxylamine upon methylchloramine (1, 169; B. 28, 1682).

Diazo-acetic ester (1, 365), diazopropionic ester (1, 371), diazosuccinic ester (1, 501), and diazomethane disulphonic acid, N C(SO₃H)₂ (1, 405), are derivatives of diazomethane.

These bodies constitute the transition to the isocyclic ring of the diazoimide or hydranoic acid, NH.

2. FOUR-MEMBERED HETEROCYCLIC SUB-STANCES.

A. MONOHETEROATOMIC FOUR-MEMBERED RINGS.

Trimethylene Oxide, CH₂ < CH₂ > O (1, 299), is a homologue of ethylene oxide. Its properties are not well known. The inner anhydrides of certain aromatic β-oxycaboxylic acids, β -lactones of the common formula \vdots C — CO \vdots C — \vdots C —

Trimethylene Imide, CH₂<CH₂>NH (1, 314), corresponding to trimethylene oxide, is produced, together with 3-methyl pyridine, on heating trimethylene dimine bydrochloride.

B. DIHETEROATOMIC FOUR-MEMBERED RINGS.

I. The most important bodies containing four-membered rings with two adjacent hetero-atoms are the cyclic salts, showing a structure analogous to that of betaine, there fore arranged under the rubric betaines. All carboxylic acids form betaines if they contain in the a-position a group similar to ammonium hydroxide. Just as trimethylglycocoll hydrochloride, ClN(CH₃)₃. CH₂. COOH, yields betaine, (CH₃)₂N - CH₁ pyridine chloracetic acid, CIN(C₅H₅)CH₄. COOII, forms pyridine betaine, $(C_3H_3)N = CH_3$ (see this); triphenylphosphine-chloracetic acid, $CIP(C_3H_3)CH_7$ COOH, triphenylphosphorbetaine, $(C_6H_5)_3P - CH_3$ (B. 27, 273), and methyl-ethyl sulphide-bromacetic acid, BrS(CH₃)CH₂. COOH, yields methyl ethyl thiobetaine, methyl ethyl thetine, $(CH_3)(C_2H_5)S - CH_3$ (I, 348).

Dimethylaziethane, $N = C(CH_3)$ (I, 328), produced on mixing equimolecular quantities of hydrazine hydrate and diacetyl, and probably also hydrazulmin and

quantities of hydrazine hydrate and diacetyl, and probably also hydrazulmin and azulmic acid (1, 437), formed by the interaction of ammonia and cyanogen, contain four-membered rings with two adjacent N-atoms.

2. The cyclic alkylidene-, carbonyl-, and thio-carbonyl-ureas, -thioureas, and +thioureas, contain rings with alternating C- and hetero-atoms:

Methylene Urea, $CO < {NH \atop NH} > CH_p$, and Methylene Thiourea, $CS < {NH \atop NH} > CH_p$ are obtained by the action of chlormethyl alcohol upon urea and thiourea (M. 12, 90); ethidene urea and -thiourea are similarly formed from acetaldehyde; methylenediphenyl- ψ -thiourea, $C_6H_5N:C<\frac{S}{N(C_6H_5)}>CH_2$, from diphenylthiourea and CH_1l_2 (p. 87); carbonyl-thiocarbanilide, $C_6H_5N:C<\frac{S}{N(C_6H_5)}>CO$, melting at 87°, from diphenylthiourea and COCl₂, as well as by desulphurizing thiocarbonyl-thiocarbanilide, C_6H_5 . N: $C < \frac{S}{N(C_6H_6)} > CS$, melting at 79°, which results from the interaction of CSC_1 and diphenylurea (B. 25, 1459).

Ĕ

3. FIVE-MEMBERED HETEROCYCLIC SUBSTANCES.

A. MONOHETEROATOMIC FIVE-MEMBERED RINGS.

Furfurane, Thiophene (Selenophene), Pyrrol.*

The members of the furfurane, thiophene, and pyrrol group contain **Ive-membered** monoheteroatomic rings. They form a closely allied **family from** the standpoint of methods of formation and chemical behavior. The parent compounds of these groups contain, in the ordinary **rense** of the term, a chain of four CH groups, which is closed as a **ring by O**, S, or NH:

The parent bodies and their numerous derivatives, especially the thiophenes, manifest a great and, in the latter instance, a very remarkable similarity to benzene and its compounds, inasmuch as many of them show the reactions peculiar to benzene derivatives in contradistinction to the fatty substances.

The production of blue-violet and violet-red dyes in the action of isatin (p. 258) and phenanthraquinone with sulphuric acid upon furfurane, pyrrol, and thiophene compounds is particularly noteworthy.

The common methods of forming furfurane, thiophene, and pyrrol derivatives from p-diketo-compounds have frequently been mentioned after the description of the latter bodies (1, 318; 11, 250, 380):

ndies (1, 318; 11, 250, 380):
Furfuranes result by the elimination of water from the y-diketones;

Phosphorus sulphide (P_2S_5) converts γ -diketones into thiophenes; Pyrrols are produced by the action of ammonia or primary amines upon γ -diketones:

$$\begin{array}{c} CH_{3}-COCH_{3}\\ CH_{3}-COCH_{3}\\ CH_{3}-COCH_{3}\\ Accionsyl Accetone \end{array} \xrightarrow{\begin{array}{c} -H_{3}O\\ \\ \\ \end{array}} \begin{array}{c} CH = C\\ \\ CH = C\\ \\ CH = C\\ \\ \end{array} \begin{array}{c} CH_{3}-CH_{3}\\ \\ CH = C\\ \\ CH_{3}-CH_{3}\\ \\ CH = C\\ \\ \end{array} \begin{array}{c} Dimethyl \ Furfurane \\ Dimethyl \ Thiophene \\ CH_{3}-CH_{3}\\ \\ Dimethyl \ Pyrrol. \end{array}$$

Here the γ -diketones react similarly to the γ -diolefine glycols. The furfuranes, the thiophenes, and pyrrols may be considered as the cyclic anhydrides, sulphides, and imides of the latter. Furfuranes, thiophenes, and pyrrols are also obtained by distilling mucic and isosaccharic acids alone or with BaS, and in the distillation of their ammonium salts.

^{*}Compare C. Paal, "Furfurane, Thiophene, and Pyrrol Syntheses," Wilrzburg, 1890.

These syntheses harmonize with the accepted structural formulas furfurane, pyrrol, and thiophene. However, experiments upon the refi tive power of thiophene render probable the presence of but one do linkage in this compound (B. 20, R. 103). A similar result was in cated by the heat of combustion of thiophene (B. 18, 1832). Hence following formulas have been proposed for thiophene, and for the an gous furfurane and pyrrol:

$$CH - CH$$
 S $CH - CH$ $CH - CH$

Many of the methods employed in making pyrrol derivatives and the ready transit under the influence of oxidants, of all three groups of substances into derivatives maleic acid (see pp. 450, 454, 458) accord very well with these formulas. See B. 1447, 1758, for formulas like

$$C \subset C$$
 s and $C \subset C$ NH.

To distinguish the possible isomerides the replaceable hydrogen atoms of the meth groups in furfuranc, thiophene, and pyrrol are designated by numbers or letters, as w benzene :

$$\begin{array}{ccc}
CII &= CH \\
CII &= CII \\
CII &= CII \\
CII &= CH \\
CII &= CH
\end{array}$$
or
$$\begin{array}{ccc}
CH &= CH \\
CH &= CH \\
CH &= CH
\end{array}$$

The positions I and 4 are equal in value; also 2 and 3. The first are also term a, the latter β -positions. It is obvious that the mono-derivatives of furfurane, th phene, and pyrrol can exist in two isomeric forms (a-derivatives and β -derivatives).

1. THE FURFURANE GROUP.*

Furfurane, Furane, C₄H₄O, boiling at 32°, was first obtained distilling barium pyromucate (p. 451) (Limpricht, 1870; C. 1897, 268): $(C_4H_3O \cdot CO_2H = C_4H_4O + CO_2)$. It is present in the distillation products of pine wood. It is a liquid, insoluble in water, and has peculiar odor. Metallic sodium has no effect upon it, nor does it con bine with phenylhydrazine. It yields dye substances with isatin and ph nanthraquinone (see above). It reacts very violently with hydrochlor acid, and forms a brown amorphous substance (like pyrrol red, p. 457 A pine shaving moistened with hydrochloric acid assumes a green col when brought in contact with the vapors of furfurane.

Brominated derivatives can be obtained from brom-pyromucic acids, or by the dire action of bromine upon furfurane. Addition products result from an excess of bromin

See C. 1897, I, 1023, for nitro- and amido-furfurane.

Methyl Furfurane, C₄H₃(CH₃)O, is in all probability sylvan, which occurs in pitar oil. It boils at 63° (B. 13, 879).

a,a₁. Dimethyl Furfurane, C₄H₂(CH₃)₂O, is formed by the distillation of carbopyrous tartaric acid (p. 451), and has been synthesized from acetonyl acetone upon heating with ZnCl₂ or P₂O₅. It boils at 94°.

^{*} Compare "Das Furfuran, etc.," von A. Bender, 1889.

It regenerates acetonyl acetone when it is heated with dilute hydrochloric acid to 170°.

2. a.e. Phenyl-methyl Furfurane, $C_4H_3\left\{ \begin{matrix} CH_3 \\ C_6H_5 \end{matrix} \right\}$ O, is produced from acetophenone-method (B. 17, 915 and 2759). It melts at 42° and boils at 235-240° C. Sodium, in is alcoholic solution, converts it into a tetrahydro-compound.

Diphenyl Furfurane, melting at 91°, is obtained from diphenacyl (B. 23, R. 743; **26**, 1447). Triphenyl Furfurane, melting at 93°, is formed from desylacetophenone (B. 21, 2933; 26, 61). Tetraphenyl Furfurane, Lepidene (B. 22, 2880), melting at 175°, is produced, together with benzil, when benzoin is heated with hydrochloric acid

Furfuro-atilbene, C₄H₅O — CH = CH — C₄H₅O, melting at 101°, is the stilbene of the furfurane series. It results upon heating polymeric thiofurfurol (B. 24, 3591).

Furfuryl Alcohol, C4H3O. CH3OH, is a colorless syrup, which is colored green by s hydrochloric acid. It results from the action of sodium amalgam and acetic acid upon # the aldehyde furfurol, but more easily by treatment with aqueous caustic potash (B. 19, 2 2154). Furfurane carboxylic acid is produced at the same time (2C₄H₃O.CHO + H₂O = C₄H₃O.CH₂OH + C₄H₃O.CO₂H) (B. 19, 2154).

Furfuryl Methyl Ether, (C₄H₃O).CH₂.O.CH₃, boils at 134-136° (B. 26, R.

Furfurylamine, C₄H₂O. CH₂. NH₂, boiling at 146°, results in the reduction of furfaronitrile (p. 450) and furfurol hydrazone (see below).

e-Furfurol, or **Furol**, $C_5H_4O_5 = C_4H_5O$. CHO, boiling at 162°, with the sp. gr. 1.163, is the aldehyde of pyromucic acid, and is produced in the distillation of bran (furfur, Fownes, 1849), or of sugar (Döbereiner, 1831), and wood, as well as most carbohydrates and glucosides, with dilute sulphuric acid. When present in even the merest traces it can be detected by the red coloration given by aniline or xylidine (B. 20, 541).

Furfurol is produced quantitatively when pentoses like arabinose, etc., are distilled with hydrochloric acid. Various analytical methods for the estimation of the pentoses are based on this fact (1, 536) (B. 28, R. 629). Glucuronic acid, when heated with hydrochloric acid, breaks down into furfurol, water, and CO, (B. 29, R. 280).

Furfurol is a colorless liquid with an aromatic odor. It is fairly soluble in water and very soluble in alcohol. It becomes brown on exposure to the air, and shows all the properties of an aldehyde. It combines with bisulphites, passes into furfuryl alcohol under the influence of sodium amalgam, and is changed to pyromucic acid by argentic oxide, and to the alcohol and acid through the action of caustic potash. It yields furfuraldoxime with hydroxylamine; this melts at 89° and boils at 205°. It unites similarly with phenylhydrazine, forming a hydrazone, melting at 96°. With orthoformic ester it yields the acetal, C₄H₂O. CH(OC₂H₅)₂, boiling at 187-190° (B. 29, 1008).

Furthermore, furfurol manifests all the condensation reactions of benealdehyde (see below). (1) It combines with dimethylaniline to form a green dye-stuff, corresponding to malachite green. (2) It condenses with aldehydes and ketones of the fatty series to furfurane aldehydes and ketones with unsaturated side-chains. This reaction occurs quite readily on digesting with dilute caustic soda (B. 13, 2342). Thus, with acetaldehyde it forms Furfur-acrolein, C₄H₃O. CH: CH. CHO, melting at 51°; with acetone, Furfur-acetone, C₄H₃O. CH: CH. CO. CH₃; with acetophenone, furfural-mono- and diacetophenone none, and Difurfural Triacetophenone (B. 29, 2248). (3) Just as potassium cyanide in alcoholic solution changes benzaldeyde to benzoln, so it converts furfurol into furcin, $C_{10}H_{5}O_{4}$, melting at 135° : $2C_{4}H_{3}O$. CHO = $C_{4}H_{5}O$. CH(OH). CO. $C_{4}H_{3}O$. This is in every way similar to benzoin. Furoin is oxidized in alkaline solution by the oxygen of the air to Furil, C_4H_3O . CO. CO. C_4H_3O . This corresponds to benzil. Tin and hydrochloric acid reduce it to desoxyfuroin, $(C_4H_3O)CH_2 \cdot CO(C_4H_3O)$ (B. 28, R. 992). Furil digested with caustic potash becomes furilic acid, $(C_4H_3O)_2C(OH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3COOH_3CO$

1

450

analogous to benzilic acid. Compare B. 25, 2843, for the condensation products of furoin with o-diamines.

(4) Furfurane acids, with unsaturated side-chains, are produced, in the condensation of furfurol and fatty acids, on heating it with the anhydrides and sodium salts of the fatty acids. This is analogous to the formation of cinnamic acid from benzaldehyde. Furfur-acrylic acid results on heating furfurane with acetic anhydride and sodium acetate:

$$C_aH_aO$$
. $CHO + CH_a$. $CO_aNa = C_aH_aO$. $CH : CH$. $CO_aNa + H_aO$.

Furfur-acrylic Acid, C7H6O3, melting at 141°, is also formed from furfur-malonic acid, the condensation product of furfurol and malonic ester (B. 24, 143; 27, 283). Furfur-acrylic acid, like cinnamic acid, occurs in an allotropic modification (B. 28, 129). The acid, when heated with hydrochloric acid, has its ring decomposed, and acetone

diacetic acid results. Sodium amalgam converts it into
Furfur-propionic Acid (1), C₄H₃O.CH₂.CH₃.CO₂H, melting at 51°. Brominewater disrupts the furfurane ring in this compound, and the product is furon-aldehyde (2), which can be gradually converted step by step into furonic acid (3), hydrofuronic acid (4), or acetone diacetic acid and pimelic acid (5):

This conversion of furfurol into n-pimelic acid proves that the aldehyde group is in the a-position.

Furfur-angelic Acid, C4H3O.CH: C(CH2.CH3). COOH, from furfurol and butyric acid, melts at 88°, and passes into the corresponding Furfur-valeric Acid under the in-

fluence of sodium amalgam.

Furfurol condenses with lævulinic acid, depending upon whether alkaline or acid solvents are employed, either to δ - or β -Furfurol-lævulinic acid, C_4H_3O . CH: CH. CO. CH₂. CH₃. COOH, or C₄H₃O. CH: C(CO. CH₃). CH₂ COOH. The latter changes readily with benzene ring-formation into aceto-oxycumarone (p. 462).

(5) Furfuramide, (C₅H₄O)₃N₂, melting at 117°, results from the action of aqueous am-

monia upon furfurol (same as hydrobenzamide from benzaldehyde, see this).

Boiling water decomposes it into furfurol and ammonia. If boiled with KOH it undergoes a transposition into the isomeric base, Furfurin, melting at 116° (compare

glyoxalines).

a-Methyl Furfurol, C₄H₂(CH₃)O. CHO, boiling at 184-186°, occurs together with furfurol in wood oil (B. 22, 608). It is also present in the product obtained by distilling varec with sulphuric acid. When rhamnose (1, 530) is distilled with sulphuric acid, it results, just as furfurol is obtained from arabinose (B. 22, R. 752).

Carboxylic Acids of Furfurane: a-Furfurane-carboxylic Acid (compare C. 1897, 11, 268), C₄H₃O. CO₂H, pyromucic acid, melting at 134° with sublimation, is obtained by the oxidation of furfurol, and in the distillation of mucic and isosaccharic acids (p. 447); it, therefore, contains the carboxyl group in the a-position.

History.—Scheele, in 1780, observed pyromucic acid as a product of the distillation of mucic acid. Pelouze (1834) determined its composition and v. Baeyer established its constitutional formula.

Its ethyl ester, C₄H₃O. CO₂. C₂H₅, melts at 34° and boils at 210° C. Its chloride, C₄H₃O. COCl, boils at 170°. Ammonia converts this into an amide, C₄H₈O. CO. NH₄,

which is changed into furfuryl-nitrile, C₄H₃O. CN, by PCl₃. The nitrile can also be obtained from furfuraldoxime by the exit of water. See C. 1897, 1, 1024, for the hydrazide, azide, etc.

Bromine vapor converts pyromucic acid into a tetrabromide, C4H3OBr4. CO4H, which is oxidized to dibromsuccinic acid by chromic acid. Fumaric acid results on evaporating pyromucic acid with bromine water. An excess of bromine or chlorine water produces mucobromic acid and mucochloric acid (1, 365).

a-Brom-pyromucic Acid, C4H2BrO. CO4H, is formed by heating the tetrabromide, and by brominating pyromucic acid in glacial acetic acid solution. It melts at 184° (B. R. 241). β-Brompyromucic Acid, from the two dibrompyromucic acids and zinc, melts at 129° (B. 17, 1759).
 Nitropyromucic Acid, C₄H₂(NO₂)O. CO₂H, melting at 183°, is formed by nitrat-

ing furfurane dicarboxylic acid and by oxidizing nitroethylene-nitrofurfurane (B. 18, 1362).

a, a₁-Furfurane Dicarboxylic Acid, C₄H₂O(CO₂H)₂, dehydromucic acid, is produced by heating mucic acid to 100° with hydrochloric acid. It dissolves with difficulty in water, and when heated breaks down into carbon dioxide and pyromucic acid.

Homologous furfurane-carboxylic acids can be obtained synthetically from γ -diketone

carboxylic esters by the exit of water.

Methylpyromucic Acid, C₄H₂(CH₂)O. COOH, melting at 109°, obtained from methyl furfurol (B. 22, 608), is decomposed by bromine water into acetoacrylic acid

 (1, 382) (B. 23, 452).
 a,a, Dimethyl Furfurane-β-carboxylic Acid, Pyrotritartaric Acid, C₄H(CH₃)₃. O. CO, H (B. 20, 1074), Uvinic Acid, melting at 135° C., may be obtained (1) from acetonyl acetoacetic ester; (2) from carbopyrotritartaric acid and from methronic acid by the splitting-off of carbon dioxide; (3) from tartaric acid by distillation; (4) from pyroracemic acid by protracted boiling with baryta-water or sodium acetate, etc.

When heated to 150-160° with steam it breaks up into carbon dioxide and acetonyl

acetone. Rapidly distilled, it decomposes into carbon dioxide and dimethyl furfurane.

 a, β_1 -Dimethylfurfurane- β -carboxylic Acid, melting at 122°, is isomeric with pyrotritartaric acid. It is formed from bromisodehydracetic acid (B. 26, 755):

(Compare the formation of coumarones from coumarine dibromides, p. 462.)

compare the formation of commandes from a compare the formation of commandes a_1a_1 -Methylphenylfurfurane- β -carboxylic Acid, $C_4H\begin{pmatrix} CH_3\\ C_8H_6 \end{pmatrix}$ O. CO₂H, from acetophenon-acetoacetic ester, melts at 181°, and when heated breaks down into CO, and

methylphenyl-furfurane (B. 17, 2764).

a,a₁-Dimethylfurfurane-β,β,-dicarboxylic Acid, C₄(CH₃)₂O(CO₂H)₂, carbopyrotritartaric acid, melting at 261°, results upon boiling diacetsuccinic ester with dilute sulphuric acid (Knorr, B. 17, 2864; 22, 146). Consult B. 27, 1158, upon isocarbopyrotritartaric acid. Carbopyrotritartaric acid at higher temperatures breaks up into carbon dioxide and pyrotritartaric acid.

Methronic Acid, C₈H₈O₅, is isomeric with carbopyrotritartaric acid. It is produced by digesting acetoacetic ester with sodium succinate and acetic anhydride (B. 18, 3410). By similar action acetoacetic ester and pyrotartaric acid yield methyl methronic acid.

Methronic acid melts at 204°.

It is also produced, together with sylvan acetic acid, poorer in CO₂ (B 21, R. 636), by the condensation of acetoacetic ester with glyoxal. Because of this method of formation, and also by virtue of its passage to pyrotritartaric acid, methronic acid has been ascribed the formula of a methyl-furfurane-acetic carboxylic acid, C4HO(CH2)(CH2.-

COOH)COOH (B. 22, 152). Compare A. 250, 166, for another view of its constitution.

Hydrofurfuranes: But few hydrofurfurane derivatives have been obtained by the reduction of furfurance—e. g., tetrahydro-a,a,-methyl-phenyl-furfurane, C,He(CH2)(Ce-H6)O, boiling at 230°, from methyl-phenyl furfurane (p. 449), tetrahydrodiphenyl furfurane

furane (B.23, R. 744), etc.

Dihydrofurfurane, C₂H₆O, boiling at 67°, may be prepared synthetically by reduci erythrol. PCl₅ converts it into furfurane (Bull. soc. chim. 35, 418).

a-Methyldihydrofurfurane, C₄H₆(CH₃)O, is obtained from acetopropyl alcol (1, 318, and B. 22, 1196). Additional dihydrofurfurane compounds have been plared synthetically from a-chlorcrotonic ester and chloriumaric ester by condensati with sodacetoacetic ester and sodium benzoyl acetic ester (B. 29, R. 859).

Tetramethylene oxide, $CH_2 - CH_2$, and its homologues (1, 299) are tetrahydr CH₂—CH₂/
furfuranes; the γ-lactones—e. g., butyrolactone, CH₂—CO

CH₂—CH₂

CH₂—CO

(I, 345)—and the a

CH₂—CO

(I, 447), etc.—are keto-si

diketotetrahydrofurfuranes. Tetronic acid, CH₂—CO

(H₂—CO

(I, 482), and its homologue are metameric with the latter.

2. THIOPHENE GROUP.*

Thiophene, C₄H₄S, an analogue in constitution of furfurane, C₄H₄O exhibits the greatest similarity to benzene. It may be viewed as benzene in which one of the three acetylene groups, CH:CH, has been replaced b By the replacement of the 4-H atoms in thiophene by other element or groups we obtain innumerable derivatives, in all respects analogous to those derived from benzene. All thiophene compounds give an intens blue coloration—the indophenin reaction, B. 16, 1473—when mixed with a little isatin and concentrated sulphuric acid.

History.—Thiophene, as well as the methylated thiophenes, are invariably associated with the benzene hydrocarbons which are prepared technically from coal-tar. There fore, before thiophene was discovered, the indophenin reaction was considered as characteristic of benzene hydrocarbons. V. Meyer (1883) observed an absence of this reaction when working with a benzene preparation made from benzoic acid, and that it reappeared when commercial benzene containing sulphur was employed in the test. This led to the discovery of thiophene. The same investigator ascertained the constitution of the latte and its kinship to furfurane and pyrrol. Thionessal, discovered by Laurent in 1841, is thiophene derivative, but it was only in 1891 that Baumann and Fromm proved it to be tetraphenylthiophene.

The synthetic methods of producing thiophene compounds from y-dicarbonyl deriva tives have been discussed (1, 318; 11, 447). The more special procedures are the reads conversion of 3 ketone acids into oxythiophenes by means of P,S₅, and thiophenes result when the primary oxythiophenes are reduced with P.S. (B. 19, 551; 23, 1495):

Thiophene, C₄H₄S, boiling at 84°, with sp. gr. 1.062 (23°), occurs in coal-tar (B. 28, 492), just as do the methyl thiophenes; indeed, the individual thiophenes are present (to upward of 0.6 per cent.) in the corresponding commercial benzene hydrocarbons, as they have the same

^{*} V. Meyer, "Die Thiophengruppe," 1888.

boiling points. Thiophene is found in benzene, methyl thiophenes in **toluene**, etc. Thiophene is also formed in considerable abundance by heating a mixture of sodium succinate and phosphorus trisulphide (Vol**hard and Erdmann**, B. 18, 454):

$$\begin{array}{cccc} CH_{a}\text{--COONa} & CH = CH \\ | & & | \\ CH_{a}\text{--COONa} & CH = CH \\ \end{array} \rangle S.$$

Thiophene also results upon heating crotonic acid, butyric acid, paraldehyde, etc., with phosphorus trisulphide: by conducting ethyl sulphide through tubes heated to redmeas or passing illuminating gas over heated pyrite, FeS, and acetylene or ethylene over boiling sulphur.

Unsaturated benzenes, when heated with sulphur, yield phenylated thiophenes. Thus, styrol forms diphenylthiophene; stilbene, tetraphenylthiophene; and acetylene dicar-boxylic acid, thiophene tetracarboxylic acid (B. 28, 1635; 30, 110). Thiophene is obtained from crude benzene by shaking it with a little concentrated sulphuric acid (4-10

per cent.) (B. 17, 792).

Thiophene is a colorless liquid, with an odor resembling that of benzene. It becomes crystalline when exposed to a mixture of solid carbon dioxide and ether. Sodium has mo effect upon it, even when it is heated. Mixed with a little sulphuric acid and isatin it becomes dark blue in color. The same occurs when its solution in sulphuric acid is dided to phenanthraquinone in glacial acetic acid (reaction of Laubenheimer, B. 19,

It is remarkable that thiophene, which from its formula cannot be regarded as a cyclic, unsaturated alkyl sulphide, does not exhibit the additive power of normal alkyl sulphides for methyl iodide, oxygen, etc. When thiophene is heated to 200° with piperidine, sulphur is eliminated and a base produced which yields tetramethylenedipiperidine, C₅H₁₀N(CH₂)4NC₆H₁₀, upon reduction (B. 28, 2217).

This very striking analogy existing between bodies of the thiophene series and the bensene series may be observed with the following representatives of both groups, the boiling and melting points of which compounds are presented in the table. The benzene derivatives have already been discussed; those of thiophene will receive attention in the succeeding pages:

BENZENE SERIES. B. P.	THIOPHENE SERIES.	В. Р.	
Benzene (p. 47),	Thiophene,	. 84° . 113° . 135° . 154° . 266° . 267° . 130° . 170° . 326°	
Benzonitrile (p. 202), 191° Acetophenone (p. 189), 202° Benzophenone (p. 345), 307° Cinnamic Acid (p. 274), m. p. 133°	Thiophen-nitrile,	. 190 . 213 . 326	

^{1.} Thiephene Homologues.—Homologous thiophenes, in addition to their synthetic formation from y-dicarbonyl compounds, are prepared from thiophene according to methods perfectly similar to those used in the production of the corresponding benzene hydrocar-

ORGANIC CHEMISTRY. bone from bentene; thus, from iodthiophene and from thiophene, alkyl bromides and al thiophene homologues, when subjected to oxidation, etc., is a chloride, etc.

e-Thiotolene, from iodthiophene by the aid of methyl iodide mi sain a-1 morosene, from iontaiophene by the aid of methyl iodide and sol verted into a-thiophenic acid by oxidation.

β-Methyl Thiophene, β-Thiotolene, is formed when sodium pyrotate with P.S.

with P.S.

Both thiotolenes occur in coal-tar.

Dimethyl Thiophenes or Thioxenes occur in crade zylese (A a 1,3-Dimethyl Thiophene bolls at 136°. 1.3-Dimethyl Thiophene bolls at 136°. 1.3-Dimethyl Thiophene bolls at 135°. 2.3-Dimethyl Thiophene bolls at 145°. 2.3-Dimethyl Thiophene bolls at 145°. It is formed when aluminium chloride acts upon a special control of the a reprepyr oromore.

a. Phenyithiophene, meking at 41°, is prepared by heating beautyl papir. (B. 19, 3140).

(B. 19, 3140).

a.a. Diphenyl Thiophene, melting at 153°, results from diphenacyl ad l from styrene or cinnamic acid with sulphur (B. 28, 890), together with a finisphene, melting at 119°. Tetraphenyl Thiophene, Thiophene, Thiophene, Thiophene, Sulphur (A. 28, 220); B. 24, 2210), inst as thiophene is framed from atheless as sulphur (A. 38, 320; B. 24, 3310), just as thiophene is formed from ethylese as

support (A. 35, 320; D. 24, 3310), just as unsupported in number are employed on plut (see above).

Dithiënyl, C₄H₂S. C₄H₂S, melting at 83° and boiling at 26°, is obtained in the property of this phase in the property of the phase is a control of substance of substance at 23°. Passible in the action of substance at a substance phenyl, by conducting the vapors or unopnesse through tunes accused to reason isomeric a,a,-Dithiënyl, melting at 33°, results in the action of sulphuris aid a thiophene and also by the interaction of a-iodthiophene and silver (B. 37, 2918).

228.2 Dishikmul Mashana (C.H.C) CH. malting at 42° and balling at 49°. thiophene and also by the interaction of a iodthiophene and silver (B. 27, 2019; 2385). Dithiënyl Methane, (C₁H₂S), CH₂, melting at 43° and boiling at 20°, Thienyl Diphenyl Methane, (C₁H₂S), Cl Thienyl Diphenyl Methane, (C₁H₂S), Cl Thienyl Triphenyl Methane, (C₁H₂S), The homologous thiophene and bendyls as readily condensed with triphenyl carbinol (B. 20, 1402). P₃O₅ acts upon triphenylcarbinol and thiophene.

Dithiënyl phenyl methane, C₂H₅. CH(C₁H₂S), melting at 75°, has been present the cold. The

22. Falogen Derivatives: Chlorine and bromine attack thiophene in the cold. The lion is even more enematic than with the heaveness. Indian in the appeared of more enematic than with the heaveness. action is even more energetic than with the benzenes. Iodine, in the presence of me a-position. In the presence of the a-position of the benzenes which below the benzenes of the a-position of the benzenes. the a-position. In properties the haloid thiophenes are very similar to the beams. When the brominated thiophenes are oxidized with strongly cooled, concertrated nitric acid, the ring is ruptured and there result dibrom-maleic acid, brom-ciracasic acid, dibromacetoacrylic acid, etc.

cid, dibromacetoacrylic acid, etc.

a. Chlorthiophene, C, H, ClS, boils at 130°, and Dichlorthiophene, C, H, ClS, at Tetrachlorthiophene, C, Cl, S, melts at 36°, and boils from 220-240°.

a. Bromthiophene boils at 150°. a, a. Dibromthiophene boils at 211°. Its faration serves for the complete isolation of all the thiophene that may be present in a mation serves for the complete isolation of all the thiophene boils at 211. Its methophene benzana /D. Prikamanthianhana malts at 20° and holls at 20°. Tetrabromthiophene (B. 18, 1490). Tribromthiophene melts at 290 and boils at 200.

It is also produced Tetrabromthiophene (B. 18, 1490). Tribromthiophene mens at a Tetrabromthiophene, C₄Br₄S, melts at 1120 and boils at 3260. a excapromethiophene, C₄Br₄S, melts at 112° and boils at 326°. It is also promound the energetic bromination of substituted thiophenes when the substituents are displaced

28, 2457).
2 lookhiophene, C.H.IS, boils at 1820.
It in order to modernta the reaction of nitric acid upon thiophene is so very energetic in order to modernta the reaction air charged with thiophene vapor is conducted (B. 17). that in order to moderate the reaction, air charged with thiophene is so very energes. See furning nitric acid Mono- and dinitrothiophene are then produced (B. 17). into the furning moderate the reaction, air charged with thiophene vapor is common state.

Mitrost, Mono- and dinitrothiophene are then produced (B. 17,

Nitrothiophene, C.H. (NO.)S, melts at 44° and boils at 225°.

Colors its alcoholic solution dark red. The same coloration of dinitrobensene, caused in the same to admixed dinitrothiophene (B. 17, 2778).

the same way, is due to admixed dinitrothiophene (B. 17, 2778).

4. Amido-derivatives: Nitrothiophene is reduced with much more difficulty than the trobenzenes. The reduction succeeds when zinc and hydrochloric acid are allowed

be act upon the dilute alcoholic solution (B. 18, 1490).

Amidothiophene, Thiophenin, C,H₂S. NH₃, is a bright yellow oil. It resinifies exposure to the air. Its HCl-salt consists of deliquescent needles. It does not yield a diazo-derivative. It combines with salts of diazobenzene, forming stable, mixed azo-dysatuffs—e.g., C₆H₅. N: N—C₄H₂S. NH₂. HCl (B. 18, 2316).

5. Sulphonic Acids: Like the benzene sulphonic acids, the thiophene sulpho-deriva-

atives are produced by dissolving thiophene in sulphuric acid. In this reaction the thiophene must be diluted with petroleum ether, benzene, or some other agent. They can also be prepared from the thionyl-ketones by displacing the ketone groups by sulpho-

can also be prepared from the thiohypercones by chaptering and the canonic by chaptering (B. 19, 674, 1620, 2623; 29, 2562).

6. Oxythiotolene, C4H₂(CH₃)S.OH, is synthetically prepared from lævulinic acid.

6. Thienylaulphydrate, C4H₃S.SH, is prepared by reducing a-thiophene-sulphonic chloride, C4H₃S.SO₂Cl. It is present in the crude thiophene product obtained by distance of the control of the cont tilling succinic acid with P2S3. It boils about 166°.

7. Aldehydes and Ketones: a-Thiophenaldehyde, C, H,S. CHO, results from the distillation of thienylglyoxylic acid. It boils at 198°. See B. 24, 47; 25, 2588, for the

thiophene aldoximes.

If oxidized, even in the air, it forms a-thiophenic acid. Aqueous caustic potash consets it into thiophenic acid and thiophene alcohol: $2C_AH_2S$. $CHO + KOH = C_AH_2$. S. CO, K + C, H.S. CH, OH.
 a-Thiophene Alcohol is an aromatic liquid, boiling at 207°.

Thiophene aldehyde condenses with sodium acetate and acetic anhydride to Thiënyl Acrylic Acid, CaHaS. CH: CH. COOH, melting at 118°. This acid corresponds to cinnamic acid.

The ketone derivatives of thiophene are obtained very easily by the action of acid

chlorides upon thiophene in the presence of aluminium chloride.

a. Thiënyl-methyl Ketone, C₄H₃S. CO. CH₃, Acetothiënone, is an oil, boiling at 213°. If it be oxidized with permanganate, it first forms Thienyl-glyoxylic Acid, C₄H₂S. CO. CO₂H, melting at 91°, and then a-thiophenic acid.

Compare B. 24, 232, R. 627, 952, for the condensation products of acetothiënone with oxalic ester. Dithiënyl Ketone, Thiënone, CO(C₄H₃S)₃, melting at 88° and boiling at 326°, is obtained from thiophene and COCl₂. Thiënyl Phenyl Ketone, C₄H₂S. CO. C₆H₃, melting at 55° and boiling at 360°, results from thiophene, benzoyl chloride, and Al₂Cl₆.

See B. 28, 1804, for the brominated thiophene ketones.

8. THIOPHENE CARBOXYLIC ACIDS.

Thiophene carboxylic acids are formed by methods which are perfectly analogous to

those employed in the preparation of the aromatic acids:

(1) By the oxidation of the alkyl thiophenes with a solution of alkaline potassium permanganate. a-Ethyl-thiophene first yields thienyl glyoxylic acid, but this changes to thiophenic acid.

(2) By the action of chlor-carbonic ester and sodium amalgam upon iod- or bromthiophene, or by the interaction of the same reagent and thiophene, or the latter, urea

chloride, and Al₂Cl₆.

a-Thiophene Carboxylic Acid, C.H.S. CO.H, melting at 126° and boiling at 260°, is also formed upon heating mucic acid with barium sulphide (p. 447).

Its nitrile, C4H₂S. CN, is produced when a thiophene sulphonic acid is distilled, or by the elimination of water from thiophene aldoxime (B. 25, 1311).

 β -Thiophene Carboxylic Acid is produced when β -methyl thiophene is oxidized. It melts at 136°.

(1,2)-Thiophene Dicarboxylic Acid, C4H2S. (CO4H), melts at 260° with decomposition. Like phthalic acid, it forms a fluorescein with resorcinol.

The (1,3)-acid melts at 1180. The (1,4)-acid sublimes at 300°. Se reduces it to

Tetrahydro-thiophene Dicarboxylic Acid, C_aH_aS(CO_aH)_p, making at the reduces ammoniacal silver solutions, capacially upon warming. It remakes the phthalic acids (B. 19, 3274) in its entire deportment.

Thiophene Tetracarboxylic Methyl Ester, C_a(COOCH_a)_aS, making at 187 obtained when acetylene dicarboxylic methyl ester is heated with sulpher to 130-150

a sealed tube (B. st, 1635).

CH-

S_CH' consists of two thiophene sucki, he Thiophthene, CH—S-C-members in common. It boils at 225°. It results when citric acid is P.S. (B. 19, 2444).

3. Selenophene.—The selenophenes are constituted analogously to the They contain an atom of selenium for sulphur. Selenophene, CH = CH/ $CH = CH \setminus$ has not yet been prepared in a pure condition. It probably is for ethide is conducted through tubes heated to redness (B. x8, x772). It probably is formed when

a,a, Dimethyl Selenophene, Selenoxene, C,H,(CH₂),Se, boiling at 153-133, produced when acetonylacetone is heated with phosphorus selenide (B. 18, 225) Isatin and sulphuric acid color it a carmine-red. It also shows the Leminater reaction (p. 453).

4. PYRROL GROUP.*

In pyrrol, C4H4N, there is a four-membered carbon chain united to a ring by the bivalent imide group. It is, therefore, a secondary amine, and, like its derivatives, possesses a feeble basic nature, as it dissolve in dilute acids. The pyrrol bodies, on the other hand, show great similarity in their behavior to the phenols; the imide hydrogen can be easily replaced by potassium. The great reactivity of the methine hydrogen in pyrrol is quite remarkable. It can be as readily, and in some instances more easily, replaced than the imide hydrogen by the most different groups and atoms. The constitution of pyrrol and its relations to furfurane and thiophene are deduced from its analogous syntheses from the y-dicarbonyl compounds.

A rather remarkable occurrence is the reversal of these syntheses—i. e., the decomposition of the pyrrol ring with elimination of the imide group. This is induced by action of hydroxylamine. Dioximes are thus produced. Thus, pyrrol yields section aldoxime (B. 22, 1968):

$$CH = CH$$

$$CH = CH$$

$$CH = CH$$

$$NH + 2H_2N \cdot OH = CH_2 \cdot CH \cdot N \cdot OH$$

$$CH_3 \cdot CH \cdot N \cdot OH + NH_3 \cdot CH \cdot N \cdot OH$$

The homologous pyrrols—e. g., a-methyl pyrrol, β -isopropyl, etc.—react similarly. This decomposition can be applied in determining the position of the substituents in the homologous pyrrols, as the a-alkyl pyrrols yield the oximes of ketones, while aldoxine are obtained from the β -substituents. These can be readily converted into dibasic acids (B. 24, R. 649, 830).

The positions of substituents in the methine groups of pyrrols are indicated, so with furfurance and thiophene, by means of numbers, 1, 2, 3, 4, etc., or letters, a, a_1 , β , β_1 etc. (compare 448).

The derivatives obtained by replacement of the imide hydrogen atom are termed s-(or N-) derivatives to distinguish them from the C-compounds.

^{*}Ciamician, "Il Pirrolo ed i suoi derivati," Roma, 1888.

Pyrrol, boiling at 131°, with sp. gr. 0.9752 (12.5°), received its name from its property of imparting a fiery red (πυβρός) color to a pine shaving moistened with hydrochloric acid. It was first found in coal-tar and bone oil (Runge, 1834; Anderson, 1858). It also is present in the distillation products of bituminous shales.

Bone oil, freed from the strongly basic substances (chiefly pyridine bases), consists of nitriles of the fatty acids, which are saponified upon boiling them with caustic potash, and in addition benzene hydrocarbons, pyrrol and its homologues. The pyrrol is contained in that portion of the oil boiling at 115-130°, which is treated with metallic potassium, whereupon solid potassium-pyrrol separates.

The oil obtained free from bone-glue by distillation is composed almost entirely of

pyrrol compounds.

Pyrrol can be obtained synthetically (1) by the distillation of ammonium saccharate or mucate, or upon heating glycerol to 200° ; (2) when acetylene and ammonia are conducted through tubes heated to redness: $2C_2H_2 + NH_3 = C_4II_4NH + II_4$; (3) from various acid imides and lactams, which may also be regarded as keto-derivatives of pyrrol hydrides. Thus, succinimide is reduced to pyrrol when it is distilled with zincdust (or sodium):

$$CH_{\bullet}$$
— CO NH H $CH = CH$ NH .

Succinimide and dichlormaleInimide, when heated with PCl₅, yield perchlorinated products, which, upon reduction, become tetrachlorpyrrol. The latter can be changed through tetraiodpyrrol into pyrrol:

Pyrrol is also produced when pyroglutaminic acid (1, 493) is heated:

$$\begin{array}{c}
CH_2-CH \longrightarrow CO_2H \\
CH_2-CO \longrightarrow CH = CH \\
CH_2-CH \longrightarrow CH = CH
\end{array}$$

$$\begin{array}{c}
CH = CH \\
CH = CH
\end{array}$$

$$\begin{array}{c}
NH.$$

Pyrrol is a colorless liquid with an odor resembling that of chloroform. It becomes brown on exposure to the air. It is but slightly soluble in water, but dissolves very readily in alcohol and ether. In yields an indigo blue coloration with isatin and sulphuric acid, or with phenanthraquinone, etc. (p. 447) (B. 17, 142, 1034; 19, 106). Pyrrol is a very feeble base. It is dissolved very slowly in the cold by dilute acids, but is rapidly resinified by strong acids. When its solutions in dilute acids are heated, ammonia is disengaged and an amorphous red powder of varying composition is precipitated. This is pyrrol red.

The resinifying action of acids upon pyrrols is probably due to polymerization changes (B. 26, 1711). Thus, dry hydrochloric acid gas precipitates (C₄II₈N)₃HCl from the ethereal solution of pyrrol. This must be regarded as the salt of a polymeric tripyrrol, (C₄H₈N)₂. Crystalline tripyrrol is obtained by neutralizing the solution of pyrrol in dilute aqueous hydrochloric acid with ammonia and then extracting with ether. Tripyrrol polymerizes further on standing, but when heated it breaks down into NH₃, indol, and pyrrol, according to the following equation (B. 27, 476):

Compare the analogous decomposition of polymeric alkyl pyrrols into alkylic in dols (p. 459).

The transition of the pyrrol ring to that of pyridine is very remarkable.

3 Chlorpyridine is formed upon heating potassium-pyrrol, or pyrrol and sodium a coholate, with chloroform:

$$\begin{array}{c}
\text{CH} = \text{CH} \\
\text{I} \\
\text{CH} = \text{CH}
\end{array}$$

$$\begin{array}{c}
\text{NK} + \text{CHCl}_{3} = \begin{pmatrix}
\text{CH} = \text{CCI.CH} \\
\text{CH} = \text{CH-N}
\end{pmatrix}$$

$$\begin{array}{c}
\text{CH} = \text{CH-N} \\
\text{CH} = \text{CH-N}$$
Brom-pyridine.

Similarly, bromoform yields β -brompyridine, and methylene chloride, pyridine, etc. I'he homologous alkyl pyrrols, when heated alone to higher temperatures, also ism pyridine derivatives.

N-Derivatives of Pyrrol: Potassium dissolves in pyrrol with an energetic evolution of hydrogen. It forms Potassium-pyrrol, $C_4H_4NK = CH = CH$ CH = CH CH = CH CH = CH

mass. This compound may also be obtained by boiling pyrrol with solid caustic potash. Water regenerates pyrrol and caustic potash. Sodium does not act like potassium. A series of N-derivatives of pyrrol may be prepared from potassium pyrrol. They are characterized by the fact that they change, on heating, to C-derivatives. This is malogous to the formation of homologous amilines from the alkylic amilines:

Alkyl iodides yield n-Alkyl Pyrrols, C₄H₄: NR, which can be directly formed if in the pyrrol syntheses primary amines be substituted for a pyrrols, and also in the distillation.

the pyrrol syntheses primary amines be substituted for ammonia, and also in the disulttion of the alkylamine salts of mucic acid, etc.

n Methyl Pyrrol boils at 113°. n-Ethyl Pyrrol boils at 131°. n-Isoamyl Pyrol

boils at 180-184°.

n-Phenyl Pyrrol, from aniline mucate, melts at 62°.

n. Pyridyl Pyrrol, C₄H₄N. C₅H₄N, boiling at 251°, is obtained from 3-amico pyridine mucate (B. 28, 1907).

With acetyl chloride the product is: n-Acetyl Pyrrol, C.H.N. CO. CH., boiling # 178°. It is also produced (together with pyrrol-methyl-ketone) upon heating pyrrol with acetic anhydride.

Phosgene converts potassium-pyrrol into n-Carbonyl Pyrrol, CO N. C.H., melt ing at 63° and distilling at 238°. When heated, it is converted into isomeric diputal ketone, CO < C₁H₃. NH:

n. Purrol Co = C₁H₃. NH:

n-Pyrrol Carboxylic Ester, C4H4N. CO2. C2H5, is formed when chlor-carbonic ester acts upon potassium pyrrol. It is an oil boiling at 180°. It passes into Pyrrol Carbamide, C, H, N . CO . NH2, if it is heated with aqueous ammonia.

n-Cyan Pyrrol, C, H, N. CN, is produced in the action of cyanogen chloride upon

potassium pyrrol. It rapidly polymerizes to a melamine derivative.

n-Anilido derivatives of the pyrrols, C4R,N. NHC6H5, have been synthetically obtained from 1,4-diketo compounds and phenylhydrazine (compare A. 289, 312).

C-Derivatives of Pyrrol: 1. C-Alkyl Pyrrols, homologous pyriols, occur in bone oil. They are artificially produced:

(a) On conducting the vapors of pyrrol and alcohols over zinc-dust: (b) Upon heating pyrrol or potassium-pyrrol with alkyl iodides. n-Alkyl pyrrols result at first, but they immediately change to c-alkyl pyrrols;

(c) By splitting off carbon dioxide from the homologous pyrrol carboxylic acids (p. 460);

(d) By direct synthesis from γ-diketones—e. g., acetonyl acetone, etc. -upon heating with ammonia.

Behavior: The C-alkyl pyrrols yield the corresponding pyrrol carboxylic acids when they are fused with caustic potash. Like pyrrol itself they are readily resinified by acids. Gaseous hydrogen chloride precipitates compounds like [C, H, (CH, NII], HCl, [C₄H₂(CH₃)₂NH]₂HCl, from the ethereal solutions of the mono- and a,β -dialkyl pyrrols. In aqueous solution dilute sulphuric acid changes these salts, with the elimination of ammonia, into alkyl indols. The reaction completes itself by the assumption of a structure for polymeric alkyl pyrrols similar to that attributed to tripyrrol (B. 24, 2562; 26, 1711):

e-Methyl Pyrrol boils at 148°, while the β -variety boils at 143°.

a.\beta-Dimethyl Pyrrol boils at 165°. These three have been obtained from bone oil. **a.\alpha_1-Dimethyl Pyrrol**, boiling at 165°, and $\alpha_1\beta_1$ -Dimethyl Pyrrol, boiling at 160°,

have been prepared from their dicarboxylic acids (p. 461).

a-Ethyl Pyrrol, boiling at 165°, and a-Isopropyl Pyrrol, boiling at 175°, are produced in the action of aldehyde or acetone and zinc chloride upon pyrrol. See B. 30, 434, for a,a,-methyl isopropyl pyrrol. a-Phenyl Pyrrol, melting at 120° and boiling at 272°, is formed by the rearrangement of n-phenyl pyrrol upon the application of heat (B. 28, 1905).

a.a. Methyl Phenyl Pyrrol melts at 101°.

Tetraphenyl Pyrrol, from bidesyl with ammonia, melts at 211° (B. 22, 553).

 a,β -Pyridyl Pyrrol, melting at 72°, is formed by the rearrangement of n,β -pyridyl pyrrol. The methyl iodide of its n-methyl ether appears to be identical with nicotyrin iodmethylate obtained from nicotine (see this) (B. 28, 1912).

2. Halogen Substitution Products: The halogens react very energetically with the pyrrol compounds. To prevent the formation of tar it is necessary to operate with very dilute solutions. Even then, as a rule, all the available hydrogen atoms of the pyrrol succleus will be immediately replaced. Chlorine and bromine oxidize pyrrol in alkaline **Solution at once and convert it into dichlor or dibrom maleInimides (p. 447). Tetrachlorpyrrol, C,Cl,NH, melting with decomposition at 110°, is also obtained**

by the reduction of the product resulting from the action of PCl, upon succinimide and dichlormaleInimide—the so-called pyrrol pentachloride, C,Cl,N, and the heptachloride, C₄Cl₄N (1, 463). It decomposes very rapidly spontaneously, and cannot be directly converted into pyrrol by retrogressive substitution. Potassium iodide converts it into iodol

(B. 19, 3027).

Iodol, Tetra-iod-pyrrol, C.I.NH, melting at 104° with decomposition, crystallizes in yellowish-brown needles. It is best made by the action of iodine upon pyrrol in the presence of alkalies. It is odorless. It is applied as an antiseptic, having the same

action as iodoform (B. 20, R. 220).
Tetrachlor-n-phenyl-pyrrol, C₄Cl₄. NC₈H₅, results when PCl₅ acts upon succinanil

3. Nitro-derivatives: Nitric acid converts pyrrol and alkyl pyrrols into resin and then oxidizes them to oxalic acid, etc. With fuming nitric acid nitro-derivatives are only obtained from the pyrrol ketones and carboxylic acids. The side-chains are sometimes

Dinitro-pyrrol, C₄H₂(NO₂)₂H₂NH, melting at 152°, is obtained from pyrrylmethyl tone. Dinitrodibrompyrrol, C₄Br₂(NO₂)₂NH, is formed from dibrompyrrol dicarboxylic acid. It decomposes very readily with liberation of NO into dibrommaleIn-

$$\begin{array}{l} CBr = C(NO_2) \\ | \\ CBr = C(NO_2) \end{array} \rangle NH = \begin{array}{l} CBr - CO \\ | \\ CBr - CO \end{array} \rangle NH + 2NO.$$

4. Pyrrol-azo-compounds: Azo- and Disazo-compounds, perfectly analogous to the benzene aso-dyes, result from the interaction of benzene diazo-salts and pyrrol or homoltine ($\kappa \delta \lambda \lambda a$) and is artificially prepared by heating carbopyrrolic acid with acetic anhydride. When it is heated with PCl₅, perchlorpyrocoll, $C_{10}Cl_6N_2O_3$, is produced. The latter absorbs eight additional chlorine atoms and passes into the chloride ($C_4Cl_7NCO)_2$, which becomes tetrachlorpyrrol upon reduction (p. 459).

β-Pyrrol Carboxylic Acid, melting at 162°, is obtained by fusing methyl pyrrol with

caustic potash.

Methyl Pyrrol Carboxylic Acids, $C_aH_a(CH_a)NH$. COOH. The a-acid melts at 169°; the β -acid at 142°. a_aa_1 -Dimethyl-pyrrol- β -carboxylic Acid, $C_aH(CH_a)_1$. NH. COOH, melts at 118°. Its ester is derived from the corresponding dicarboxylic

esters by the exit of carbon dioxide.

 a_1a_1 -Diphenylpyrrol Carboxylic Acid, $C_4H(C_4H_5)_3NH$. COOH, melting at 261°, is obtained from phenacylbenzoylacetic ester, C_6H_6 . CO. CII(CO₂R)CII₂. CO. C_6H_6 (p. 381). a_1a_1 -Pyrrol Dicarboxylic Acid, $C_4H_3NH(COOH)_9$, from carbopyrrol glyoxylic acid (p. 461), decomposes at 200° into carbon dioxide and pyrrol. a_1a_1 -Dimethyl- $\beta_1\beta_1$ -pyrrol Dicarboxylic Acid, $C_4(CH_3)_3NH(COOH)_9$, from diacetosuccinic ester, breaks down at 251° into 2CO₂ and a_1a_1 -dimethyl pyrrol. $a_1\beta_1$ -Dimethyl- β_1 -pyrrol Dicarboxylic Acid, from acetoacetic ester with isonitrosoacetoacetic ester, decomposes at 197° into 2CO₂ and $a_1\beta_1$ -dimethyl pyrrol. a_1 -Diphenyl- β_1 -pyrrol Dicarboxylic Ester, melting at 152°, is produced when ammonia acts upon dibenzoyl succinic ester (A. 293, 107).

Pyrrolen-phthalide, $CO < {}^{C}_{O}{}^{H_4} > C < {}^{C}_{NC_4H_3}{}^{H_3} > C < {}^{C}_{O}{}^{H_4} > CO$, is produced when phthalic anhydride and pyrrol are heated together (B. 19, 2201). Its formula is

probably analogous to that of pyrocoll.

Hydropyrrol Derivatives: When pyrrol is reduced (zinc-dust and acetic acid) two hydrogen atoms are added and dihydropyrrol or pyrrolin, C₄H₇N (1, 314), is produced. Further addition of hydrogen (by means of HI and phosphorus) leads to tetrahydropyrrol or pyrrolidine, C₄H₂N. The nature of pyrrol is very essentially altered by this addition of hydrogen. Whereas pyrrol is a very feeble base, pyrroline and pyrrolidine, to even a greater degree, manifest the strong basic properties of the secondary amines of the aliphatic series.

Pyrroline, $CH_2 - CH_2$ NH, is a liquid that dissolves readily in water and boils at 91°. It has an alkaline reaction, smells like ammonia, and unites with acids to form salts. It is a secondary base. Nitrous acid converts it into nitrosamine, $C_4H_8N(NO)$, melting at 38°.

Pyrroline and methyl iodide unite to dimethyl-ammonium iodide, C₄H₆N(CH₃)₂I.

n-Methyl Pyrroline, C₄H₆N. CH₃, is formed by the reduction of methyl pyrrol. In boils at 80°.

Pyrrolidine, Tetramethylene-imine, $CH_2 - CH_2 > NH$, as well as its homologues,

have already been described in connection with the aliphatic bodies. In addition to the methods there given for its production another may be introduced at this point. It represents a transition of the six-membered piperidine ring into the five-membered pyrrolidine ring. Piperidine or pentamethylene-imine combines with alkyl iodides, forming dimethyl-piperidinium iodide, the hydroxide of which, upon distillation, changes to a compound with an open chain, butallylcarbindimethylamine. The hydrochloride addition product of the latter readily rearranges itself into the chlormethylate of n,a-dimethylpyrrolidine:

Other unsaturated amines analogous in constitution to butallylcarbindimethylamine can be changed by HCl to pyrrolidine bases (Merling, A. 264, 310; 278, 1). Pyrrolidine can be carried through changes similar to those indicated above for piperidine. It

may be combined with methyl iodide. The resulting dimethylpyrrolidylium iodide c then be decomposed by distillation with caustic potash, and the base dimethyl pyrrolidir C4H7N(CH2)2, will be obtained. When its iodmethylate is distilled with potash t products are trimethylamine and an unsaturated hydrocarbon, Pyrrolylene, C.H. (B. 1

n-Methyl Pyrrolidine, C₄H₈N. CH₃, boiling at 81-83°, is identical with the bas which is produced by the elimination of carbon dioxide from hygric acid or n-methy pyrrolidine carboxylic acid, an oxidation product of the alkaloid hygrine present coca leaves (B. 30, 1113). a,2-Pyridyl-n-methyl Pyrrolidine is very probably tl alkaloid nicoline. Consult B. 30, 1588, for the reduction products of a,a,-dimethyl pyra

Netopyrrolidines or Pyrrolidones are the lactams of the y-amido-acids, like Butyn CH₂—CO NH, which have also been discovered in conne CH₂—CH₂—CH₂

tion with the aliphatic bodies.

Diketopyrrolidines are the imides of the succinic acid series—e. g., succinimide CH₂—CONH (1, 448). a,β-Diketopyrrolidines are produced in the condensation o oxalacetic ester with benzalanilines—e. g., a,β -diketo-n, a_1 -diphenyl- β_1 -pyrrolidin carboxylic ester, C_6II_5N CO CH(C_6H_5)—CH(CO_2R), melting at 171° (B. 30, 602)

Xanthoxalanil, $CO - CO N \cdot C_6H_5$ (B. 24, 1252), the anil of oxalacetic acid, is triketo-pyrrolidone.

CONDENSED NUCLEI OF THE FURFURANE, THIOPHENE, AND PYRROL GROUPS.

When two adjacent C-atoms of a furfurane, thiophene, or pyrro nucleus participate in the formation of a benzene, naphthalene, etc., group, condensed nuclei result, which sustain the same relations to the simple heterocyclic rings that the condensed nuclei of the naphthalene, phenanthrene, and anthracene groups bear to benzene.

The following condensed nuclei are derived from furfurane, thiophene, and pyrrol:



Benzofurfurane, Coumarone



Dibenzofurfurane, Diphenylene Oxide





Dibenzothiophene Diphenylene Sulphide



Benzopyrrol, Indol



Dibenzopyrrol, Diphenylene-imide, Carbazole.

The dicyclic nuclei can have place-isomeric combinations:





These are designated isobenzofurfurane, isobenzothiophene, and isobenzopyrrol or isofndol. These hypothetical parent substances give rise to a series of substances which have been discussed in conjunction with compounds having open chains. From isobenzofurfurane we may consider as derivatives: tetrachtorxylylene oxide (p. 232), phthalic anhydride (p. 240). To isobenzothiophene may be referred: xylylene sulphide (p. 232), thiophthalide (p. 235), thiophthalic anhydride (p. 240); to isoIndol: xylyleneimine (p. 232), phthalimidine (p. 234), and phthalimide (p. 240). To isoIndol may also be referred methyl isoIndol, C₆H₄ C(CH₂) N, derived from phthalazine (B. 26, 710).

Condensed nuclei further are known in which two heterocyclic rings also participate in the formation of a benzene nucleus—e. g., benzodifurfurane and benzodipyrrol derivatives

(p. 464).

Coumarone and indol should be especially mentioned as the parent substances of important groups. Indol is the mother substance of indigo. These two bodies will be considered together with benzothiophene. Next will follow the groups of dibenzo-compounds: diphenylene oxide, diphenylene sulphide, and carbazole.

5. BENZOFURFURANE or COUMARONE GROUP.

The coumarone compounds, as their name would imply, are produced:

(1) By the action of alcoholic potash upon commarine dibromides or a-brom-commarines (Fittig, A. 216, 162):

Other coumarines react similarly—e. g., umbelliferone, æsculetine, and daphnetin. It is very certain that a-brom-o-oxycinnamic acid and its homologues occur as intermediate products. These split off HBr and form the coumarone ring. The formation of benzoyl coumarone, C₈H₆CH OC. COC₈H₈, from aceto-o-oxybenzalacetophenone dibromide and caustic potash, as well as by the condensation of salicylaldehyde by means of a homometophenone and caustic potash, proceeds analogously (B. 20, 227 R. 200)

of & bromacetophenone and caustic potash, proceeds analogously (B. 29, 237, R. 290).

(2) Other o-disubstitution products of benzene combine to yield a coumarone ring.

Caustic potash converts o-oxychlorstyrene into coumarone (B. 26, R. 678):

$$C_eH_e < CH = CHCI \longrightarrow C_eH_e < CH CH.$$

(3) By heating o-aldehydo-phenoxy-acetic acid with sodium acetate, coumarilic acid results (B. 17, 3000):

$$C_{\bullet}H_{\bullet}$$
 $C_{\bullet}H_{\bullet}$
 $C_{$

(4) The synthesis of aceto-oxycoumarone, however, from furfural- β -lævulinic acid represents a benzene ring formation (B. 26, 345):

(5) By the action of zinc chloride upon phenoxylacetals and their homologues (B. 3) 1700):

$$C_0H_4 \stackrel{H}{\swarrow}_{OCH_1.CH(OC_2H_1)_3} \longrightarrow C_0H_4 \stackrel{CH}{\swarrow}_{O}CH.$$

(6) Just as the coumarines are formed from phenol and malic acid or acetoacetic ester so the coumarones are obtained from the sodium salts of the phenols with a-chloraceto acetic ester (Hantzsch, B. 19, 1291):

Resorcin and two molecules of the ester yield a benzodifurfurane, pyrogallol with three molecules of the ester form a benzotrifurfurane, while a naphthofurfurane is obtained

A perfectly similar reaction is noticeable in the production of coumarone and benzodifurfurane derivatives from quinones and chlorinated quinones—e. g., chloranil, when

heated with acetoacetic ester (J. pr. Ch. [2], 45, 67; A. 283, 245).

Coumarone, C₆H₆O, boiling at 169°, is formed by distilling coumarilic acid with lime. It is obtained from 0-0xy-w-chlorstyrene; from phenoxylacetal with zinc chloride (B. 30, 1703), as well as from coal-tar (B. 23, 78). Concentrated acids convert it into a resin. With bromine it yields a dibromide, melting at 88°. Sodium and alcohol reduce it to dihydrocoumarone, coumaran, CaH₈O, boiling at 189°, together with ethyl phenol (B. 25, 2409).

β-Methyl Coumarone, C₉H₈O, from methyl coumarilic acid, boils at 189°.

a, 3 Dimethyl coumarone, from dimethyl coumarilic acid, boils at 210°.

a Benzoyl Coumarone, C₈II₅O(COC₆H₅), melting at 91°, obtained from acetylo-oxybenzalacetophenone dibromide, as well as in the condensation of salicylaldehyde with phenacyl bromide, is decomposed by fusion with caustic potash into coumarone and benzoic acid (B. 29, 237, R. 290).

a-Coumarilic Acid, C₈H₅O. COOH, melting at 190°, is obtained from a-brom-

coumarine. Sodium amalgam converts it into hydrocoumarilic acid, CaHaOa.

β-Methyl-a-coumarilic Acid melts at 189°. Its ethyl ester is produced on heating sodium phenoxide with acetoacetic ester (see above). It melts at 51°.

melting at 258°, is prepared from chloranil and acetoacetic ester.

β-Ketocoumaran, Ketodihydrocoumarone, C₆H₄< CO>H, melting at 97°, is made from aceto-o-oxyacetophenone bromide (B. 30, 1081).

Benzodimethyldifurfurane Dicarboxylic Ester,

Benzodimethyldifurfurane Dicarboxylic Ester,
$$CO_{2}R. C = CCH_{3}C C_{6}H_{2} C. CO_{2}R, \text{ is obtained from resorcinol and chloracetoacetic ester.} C. CO_{2}R, \text{ is obtained from resorcinol and chloracetoacetic ester.} The a-compound melts at 186° and the β -body at 141°. Benzotrimethyltrifurfurane Tricarboxylic Ester, $C_{6}C. CH_{3}$, is similarly formed$$

from phloroglucin. It melts with decomposition at 297'

Naphthofurfurane, $C_{10}H_6[C_1H_2O]$, melting at 61° , is made by the action of ZnCl, upon naphthoxylacetaldehyde, $C_{10}H_2O$. CH₂. CHO, dissolved in glacial acetic acid (B.

30, 1702). Naphthomethylfurfurane Carboxylic Ester, C₁₀H₆C.CO₂R, melting at 110°, is obtained from a-naphthol and chloracetoacetic ester.

Naphthoketocoumaran, C₁₀H₆(C₁H₂O₁), melting at 92°, is formed from 2-bromaceto-I-acetylnaphthol (B. 30, 1468).

6. BENZOTHIOPHENE GROUP.

Benzothiophene is produced from a-sulphhydryl-ω-chlorstyrene, which has only been smalled in the form of its xanthogenic ester. This is analogous to the formation of commarone from 0-oxy-ω-chlorstyrene (B. 26, 2809):

$$C_0H_4 \stackrel{CH = CHCl}{\longleftrightarrow} C_0H_4 \stackrel{CH}{\longleftrightarrow} CH_5$$

which is similar to the formation of acetoxycoumarone from the condensation product of forfurol and lævulinic acid.

Oxybenzothiophene results from the condensation of thiophenaldehyde with succinic **scid (B. 19,** 1619):

$$\textbf{C_4H_2S} \begin{cases} [\beta] \text{H} & \text{HOOC.CH_3} \\ [a] \text{CHO} & \text{H_3C-COOH} \end{cases} \rightarrow \textbf{C_4H_3S} \begin{cases} [\beta] \text{C(OH)} = \text{CH} \\ [a] \text{CH} & \text{CH_2O} + \text{CO_3O} \end{cases}$$
 Thiophenaldehyde Succinic Acid 4-Oxybenzothiophene.

Benzothiophene, Thionaphthene, C₈H₆S, melting at 31° and boiling at 221° (C. 2897, II, 270), has an odor like that of naphthalene. 4-Oxythionaphthene, C₈H₆. (OH)S, melting at 72°, resembles a-naphthol in its behavior (compare thiophene).

BENZPYRROL OR INDOL GROUP.

The most important substances belonging in this group have been obtained from indigo-blue, to which the indol derivatives bear an intimate kinship. Indol, and especially the methyl indols, as derivatives of pyrrol, show most of the reactions of the latter (B. 19, 2988). By a rupture of the ring the indol bodies are converted mainly into orthoamido-acids of benzene. Our knowledge of the constitution of indol and its derivatives, and their relations to indigo, is based chiefly upon the investigations of A. v. Baeyer (p. 473).

Indol, $C_8H_7N=C_8H_6$ CH CH CH (a), melting at 52° and boiling at 245° with decomposition, is obtained:

(1) By the distillation of oxygen-containing derivatives—e. g., oxindol (p. 471),

indigo blue (p. 473)—with zinc-dust.

(2) By condensation of various o-amido-substitution products of benzene, or by the (2) By condensation of various o-amido-substitution products of benzene, or by the reduction of o-nitro-compounds; for example, the action of sodium alcoholate upon o-amidochlorstyrene (p. 207), C_6H_4 CH = CHCl CH₂ CH₃ CH₄ CH₄ CH₄ CH₅ analogous to commarone (p. 463) and benzothiophene (above); also by the reduction of o-nitro-phenylacetaldehyde or o-nitrocimnamic acid, C_6H_4 CH₂. CHO CH₂. CHO C₆H₄ CH₅ CH₅

COOH, and calcium formate proceeds in a similar manner (B. 23, R. 654).

(3) The pyrogenic formation of indol from alkylic anilines, tetrahydroquinoline, and especially from cumidine when the vapors are conducted through tubes heated to red-

ness, are due to ortho-condensations.

(4) Finally, indol is formed (together with skatole—see this) from albuminate in the pancreatic fermentation (method of production), or when they are fused with caute potash.

Behavior: Indol crystallizes from water in shining leaflets. It posesses a peculiar odor, resembling that of naphthylamine, and is readily volatilized in aqueous vapor. Its vapor density (under diminished presure) corresponds to the formula C.H.N. A pine splinter moistened with hydrochloric acid and dipped into its alcoholic solution or the vapors acquires a cherry-red color. Indol possesses but very feeble basic properties (similar to pyrrol), and is easily resinified by acids.

With picric acid it forms a compound which crystallizes in red

needles.

The substituents of indol in the pyrrol ring are termed a-, β -, n-, or Py(1,2,3); those

in the benzene ring, 1,2,3,4 or Bz(1,2,3,4) (A. 236, 121).

n Nitrosoludol, C, H₈N. NO, melting at 172°, formed from indol and sodium nitrie, probably has the doubled formula (C. 1891, 11, 62). Various acetyl indols are produced. when indol and acetic anhydride are heated together (B. 23, 1359, 2296).

Homologous Indols are produced: 1. Like indol from o-amido-compounds of the benzene series by the formation of closed rings:

Similarly, o amido-desoxybenzoin yields a phenyl indol and o-methylamido-e-chla-

styrene: n methyl indol.

2. By heating the anilines with compounds containing the group CO. CHCl. For example, aniline and chloracetone yield a-methyl indol; with 3-bromlevuline and a 4-dimethyl indol is the product. A simultaneous evolution of CO, occurs here. This reaction is parallel to that of the so-called quinaldine synthesis. For its course see B. 25. 2800; 26, 1336, 2638. Aniline and bromacetophenone yield a-phenyl indol.

3. A noteworthy method for the production of the alkyl indols consists in condensing the phenylhydrazones of the aldehydes, ketones, and ketonic acids by heating them with hydrochloric acid or zine chloride (E. Fischer, B. 19, 1563; 22, R. 14), when ammonia is split off:

$$\begin{array}{c} \text{CH}_{5}. \text{ NII}. \text{ N}: \text{CH}_{2}. \text{CH}_{3} & \text{C}_{6}\text{H}_{4} & \text{CH}_{2}\text{CH}_{3} \\ \text{Propylidene-phenylhydrazone} & \beta\text{-Methyl Indol} \\ \text{C}_{6}\text{H}_{5}. \text{ N}(\text{CH}_{3}) \text{N}: \text{C}_{\text{CH}_{3}}^{\text{CH}_{3}} & \text{C}_{6}\text{H}_{4} & \text{N}(\text{CH}_{3}) \\ \text{Acetone-phenylmethylhydrazone} & \text{N}_{(\text{CH}_{3})} & \text{C}_{C}\text{CH}_{3} \\ \text{C}_{6}\text{H}_{5}. \text{NII}. \text{N}: \text{C}_{\text{C}}^{\text{CH}_{3}} & \text{C}_{6}\text{H}_{4} & \text{C}_{\text{C}}\text{CO}_{2}. \text{R} \\ \text{Phenylhydrazone-pyroracemic} & \text{C}_{6}\text{H}_{4} & \text{C}_{\text{C}}\text{CO}_{2}. \text{R} \\ \text{Ester (p. 124)} & \text{a-Indol-carboxylic Ester.} \end{array}$$

The unsym. alkylphenylhydrazine derivatives react very easily with pyroracemic acid; the upon warning them with dilute hydrochloric acid, sulphuric or phosphoric acid; the acids are n-alkyl-indol-carboxylic acids.

The phenylhydrazones of the \(\theta\)-ketonic scores of the \(\theta\)-ketonic acids. Some, when heated with concentrated sulphuric acid, yield indol compounds (B. 27, R.

793). This is especially true of the unsym. alkylphenylhydrazones. See also indol-

2008, p. 470.4. The polymeric alkyl pyrrols upon standing with dilute sulphuric acid part with **emmonia** and pass into alkylic indols—e. g., tetramethyldipyrrol changes to $a,\beta,2,3$ tetramethyl indol.

Behavior: The alkyl indols substituted in the pyrrol nucleus possess generally the fæcal odor, and can be distilled without decomposition. The phenyl indols and indol carboxylic acids are non-volatile and odor-They are more stable toward acids than indol, dissolve in concentrated acids, and are reprecipitated unaltered by water. Picric acid unites with all of them, forming compounds crystallizing in red needles. Most of the indol derivatives give the pine-shaving reaction, the exceptions being the indol carboxylic acids and the α, β -dialkyl indols. The alkyl indols, like the alkyl pyrrols, yield indol carboxylic acids when they are fused with caustic potash.

The indols, like pyrrol, combine with aldehydes, acid anhydrides, and diazo-compounds, hydrogen atoms of the pyrrol nucleus being replaced by the acidyl, the diazo-group, etc. Red dyestuffs, resembling fuchsine and called rosindols (B. 20, 815), are produced by heating various indols with benzovl chloride and zinc chloride.

The behavior of indol by exhaustive methylation is remarkable; all of the hydrogen atoms of the pyrrol nucleus are replaced by methyl, and then by the further action of methyl iodide a body results which formerly was thought to be a dihydro-n,a, y-trimethylquinoline, because its corresponding reduction product, a tetrahydro-base, could be changed to a, γ -dimethyl-quinoline. However, the so-called dihydrotrimethyl quinoline is reconverted by the distillation of its iodhydrate into a, β -n-trimethyl indol, and when oxidized with chromic acid or potassium permanganate yields β , β -dimethyl-a-indolinon, so that formulas like the following have been suggested:

$$C_{\text{g}}H_{\text{e}} \underbrace{ \begin{matrix} C(CH_{\text{g}}) - CH_{\text{g}} \\ \\ N(CH_{\text{g}}) - C(CH_{\text{g}}) \end{matrix}}_{\text{l}} \quad \text{or} \quad C_{\text{g}}H_{\text{e}} \underbrace{ \begin{matrix} C(CH_{\text{3}})_2 - CH \\ \\ N(CH_{\text{g}}) - CH \end{matrix}}_{\text{l}} (\text{B. 2g, 2460}).$$

Compare B. 21, 1940, for the conversion of the indols into quinolines by means of

chloroform and sodium alcoholate.

n. Methyl Indol, $C_8H_8N(CH_3)$, boiling at 239°; n-Ethyl Indol, boiling at 247°; Allyl Indol, boiling at 252° (B. 26, 2174); and n-Phenyl Indol, $C_8H_8N(C_8H_5)$, are obtained from their carboxylic acids by the elimination of carbon dioxide. Bromine in sodium hydroxide oxidizes n-methyl and n-ethyl indol to methyl and ethyl-w-isatin (p. 472).

a-Methyl Indol, C₀H₆(CH₂)NH, Methyl Ketol, arises from o-amido-benzylmethyl ketone, and acetone phenylhydrazone. It melts at 59°. Its odor is like that of indol, and its reactions are similar. Oxidation with MnO₄K (by rupture of the pyrrol ring at the point of the double binding) converts it into o-aceto-amido-benzoic acid:

$$C_8H_4$$
 C_8H_4
 C

a-Indol carboxylic acid is formed when it is fused with caustic potash.

β-Methyl Indol, Skatole, C₈H₈(CH₉)NH, occurs in human faces (with a little indol). It may be obtained, together with indol, from reduced indigo, by the putrefaction of albuminoids, or (with indol) in the fusion of the same with potassium hydroxide. It can be prepared without difficulty by heating propidene-phenylhydrazone with zinc chloride. It melts at 95° and boils at 265°. It has a penetrating faceal odox.

E. E. Trimethyl Indol boils at 280° (see above). $a,\beta,2,3$ -Tetramethyl Ind (CH₃ 2C₆H₄: [C₂,CH₃),NH], melts with decomposition at 285° (B. 22, 1924). I obtained from tetramethyldipyrrol (p. 458). e-Phenyl Indol, CaHa(CaHa)NH, m consists from terrametaryampyros (p. 450). a-rawinys 1800s, Cgrig(Cgrig)NH, in ing at 187°, has been prepared from acctophenous phenylhydrasune, from o-nitrod oxybenzoin, from bromacetophenous and sailine (see above), and, lastly, by the rearms ment of ,3-Phenyl Indol, CgHg(CgHg)NH, melting at 89°, supon heating it to 1; with zinc chloride (B. 21, 1811). Similar rearrangements are manifested by the different methyl phenyl indols (B. 22, R. 44). a-Thillayl Indol, melting at 162°, a a-Naphthyl Indol, melting at 196°, are obtained from the phenylhydrasones of natheless of this originated by the difference (B. 25, B. 24). thyl and thirnylmethyl ketones (B. 26, R. 44).

The chlorine substitution products of the indels are produced by the action PCl₂ upon their oxygen-containing derivatives—e. g., a,β-dichlorindel, C₂H₂C₂N

melting at 104°, from oxindol (p. 471).

3. Sulphoacids of the indols, containing the sulpho-group in the pyrrol-nucle have been synthesized from methyl and ethyl sniline by condensation with glyazal bis phile (1, 321) (B. 27, 3258):

n-Methyl Indol-e-Sulphonic Acid, C,H, C. SO,H, on being boiled wi

hydrochloric acid, splits off SO, very readily and becomes n-methyl exindel. Th naphthylamines and alkylic naphthylamines react like the alkylic anilines with glyon bisulphite.

4. Indel Carboxylic Acids.

These are produced (1), in addition to the synthetic method, from the phenylhydra zones of the pyroracemic acids, by reactions perfectly similar to those employed for the pyrrolcarboxylic acids; (2) when the indols are heated with sodium and carbon dioxide (3) by fusing the alkyl indols with caustic alkali. Ordinary oxidizing agents do not attact them (B. 21, 1925). Heated alone or with lime, they break down into carbon dioxid and indols.

a Indol Carboxylic Acid, C.H.N. CO.H, melting at 200° with decomposition, he been prepared from pyroracemic phenylhydrazone, from a-methyl indol by the potasi

fusion, and by the latter process from tetrakydrocarbasele.

The acid also results in the reduction of o-nitrophenyl pyrorscemic acid with zine-dust and glacial acetic acid, whereas the product will be n-oxyindolcarboxylic acid when sodium amalgam is used (see p. 469 and B. 30, 1045). It yields an imide anhydride (B. 22, 2503) corresponding to pyrocoll if heated with acetic anhydride.

3-Methyl-a-Indol Carboxylic Acid, C₈H₈(CH₉)N. CO₂H, shatole carboxylic acid, results from the decay of albuminates. It melts at 155°. Another product, formed at the same time, is Skatole Acetic Acid, C₈H₈(CH₉)N. CH₂. CO₂H, melting at 134° (B. 20. P. 201).

(B. 22, R. 701).

β Indol Carboxylic Acid, CaHaN. COaH, is produced when skatole is fused with caustic potash, and upon heating indol with sodium in a current of carbon dioxide. It melts with decomposition at 218°. It does not yield an imide anhydride (B. 23, 2296).

n-a-Dimethyl-indol-β-carboxylic acid, C₂H₄(CH₃)N(CH₃). COOH, from methyl-phenyl-hydrazone acetoacetic ester, C₅H₅N(CH₃). N: C(CH₃). CH₃. CO₄R, melts at 200°.

5. Oxvindol Derivatives: Indoxyl, β-Oxyindol, C₆H₄COH)

CH, from in-

5. Oxyindol Derivatives: Indoxyl, β-Oxyindol, C₆H₄

doxylic acid by the elimination of CO2, and from indigo by fusion with caustic potash away from air (B 26, 225), is an oil easily soluble in water, with a yellow fluorescence. It is very unstable and is readily resinified. It dissolves with a red color in concentrated hydrochloric acid. It is oxidized to indigo blue when its alkaline solution (best ammoniacal) is exposed to the air. Ferric chloride and hydrochloric acid effect the conversion more quickly:

 ${}_{2}C_{6}H_{7}ON+2O=\underset{\text{Indigo Blue.}}{(C_{8}H_{8}NO)_{2}}+2H_{2}O.$

When indoxyl is digested with potassium pyrosulphate, S₂O₇K₂, we get potassium indoxylsulphate, CaHaN.O.SOaK, which is found in the urine of herbivorous animals (Urine indican), generally after the ingestion of indol. When digested with acids the salt decomposes into sulphuric acid and indoxyl, which forms indigo blue by the addition of a little ferric chloride. We proceed similarly in the detection of indoxylsulphuric acid in urine.

This potassium salt may be synthesized by fusing o-phenylglycocoll-carboxylic acid with caustic potash, and subsequently treating with potassium pyrosulphate. If the potassium hydrate fusion be treated with benzyl chloride, n-Benzyl- β -benzyl-oxyindol, melting at 166°, is produced (C. 1897, I, 862).

Indoxylic Acid, $C_9H_7NO_5 = C_9H_4 < C_0O_1 > C_0O_2 II$, a carboxylic acid of in-

doxyl, is produced from its ethyl ester by fusion with caustic soda (B. 17, 976). It melts at 123°, with decomposition. Its ethyl ester is obtained by reducing o nitrophenyl propiolic ester with ammonium sulphide, or isatogenic ester, and from indoxanthic ester, which is an intermediate product in this reaction, and can be obtained by oxidizing the ester of indoxylic acid:

When digested with sulphuric acid it affords a quantitative yield of indigo-sulphonic acid. It possesses a phenol character, which is indicated by its solution in alkalies, acis. It possesses a phenoi character, which is indicated by its solution in alkalies, from which it is again precipitated by carbon dioxide. Ethyl iodide converts the salts of indoxylic ester into ethyl indoxylic ester, $C_8H_6(OC_2H_5)N \cdot CO_3R$, which by saponification with baryta water, forms Ethyl-indoxylic Acid. This acid loses CO_3 when it is heated, and becomes ethyl indoxyl, $C_8H_6(OC_2H_5)N$, which resembles indo in its chemical behavior and in its odor. When digested with hydrochloric acid, ethyl indoxylic acid yields indoxyl, and by nitrous acid is converted into pseudoisatoxime (p. 472). In many reactions indoxyl, as well as indoxylic acid, yields products which are derived from pseudoindoxyl, or dihydro- β -ketoIndol, an isomeride of indoxyl, so that it may be assumed that in these instances

may be assumed that in these instances

In the second form indoxyl and indoxylic acid react with aldehydes, ketones, and ketonic acids,-e. g., benzaldehyde, pyroracemic acid, etc.,-with the production of socalled indogenides. The bivalent group, $C_6H_4 < {CO \atop NH} > C =$, is termed indogen (B. 16, 2197):

$$\begin{array}{ll} \text{C}_{6}\text{H}_{4} < \stackrel{CO}{N} > \text{C} = \text{CH} \cdot \text{C}_{6}\text{H}_{5} & \text{C}_{6}\text{H}_{5} < \stackrel{CO}{N} > \text{C} = \text{C}(\text{CII}_{5})\text{CO}_{2}\text{H} \\ & \text{Indogenide of Benzaldehyde} & \text{Indogenide of Pyroracemic Acid.} \end{array}$$

Isatin and benzene hydrocarbons also yield indogenides. Isatin may be viewed as indogen exide. Isatin converts indoxyl (B. 17, 976) into the indogenide indirubin (p. 476):

$$\begin{array}{c} \textbf{C_0H_4} < \begin{matrix} \textbf{CO} \\ \textbf{NH} \end{matrix} > \textbf{CH_2} + \textbf{OC} < \begin{matrix} \textbf{C_0H_4} \\ \textbf{CO} \end{matrix} > \textbf{NH} \longrightarrow \textbf{C_0H_4} < \begin{matrix} \textbf{CO} \\ \textbf{NH} \end{matrix} > \textbf{C} = \textbf{C} < \begin{matrix} \textbf{C_0H_4} \\ \textbf{CO} \end{matrix} > \textbf{NH} \\ & & \textbf{Indirabin.} \end{array}$$

which is isomeric with indigo blue. The latter is also produced by the oxidation of a doxy. (p. 405); hence it may be viewed as diindogen:

$$C_{\bullet}H_{\bullet} < \stackrel{CO}{>} C = C < \stackrel{CO}{>} C_{\bullet}H_{\bullet}$$
Indigo Biue (Diindogen).

3. Ethoxy-a-methyl Indol, C₂H₃N(O, C₂H₃)(CH₃), melting at 142°, is obtained from ethoxyacetonephenylhydrazone, C₄H₃NIN: C(CH₃)CH₂OC₄H₃ (B. 25, R. 47).

10. Oxyindol a carboxylic Acid, melting at 159° with decomposition, is independent of the composition of

with indoxylic acid. It results on boiling o-nitrobenzylmalonic acid with some hydroxide:

 $C_6H_4 \xrightarrow{NO_3} C_6H_4 \xrightarrow{N(OH)} C(COOH)_1$

as well as by the reduction of o-nitrophenylpyroracemic acid with sodium amaigun. It is readily reduced to a indol carboxylic acid. Potassium permanganate oxidizes it, when the possible intermediate production of phenylhydroxylamine-o-carboxylic acid, to o azoxybenzoic acid, while with chromic acid it yields isatin. It can be very easily

acidylated or alkylized in the NOH group.

10. Methoxyindol a carboxylic Acid, melting at 185° with decomposition, is also reduced to indolcarboxylic acid, and oxidized by chromic acid to n-Methoxy constitution, C₆H₄ CO CO, consisting of red needles, melting at 110°. Bleaching line, hydrogen peroxide, etc., convert n-oxyindolcarboxylic acid into indoxin. This is a blue-colored, unstable dye, very similar to indigo, but soluble in alkalies. When it is dissolved in concentrated sulphuric acid and the diluted solution is allowed to sund

exposed to the air, indigo separates. The yield is good (B. 29, 639; 30, 1045, 1055) a. Phenyl-oxyindol, C₁H₃N(C₆H₅)(OH), melting at 175°, is formed in the action of concentrated sulphuric acid upon benzoln oxime. It is doubtful whether in this derivative the hydroxyl group is attached to the nitrogen or to one of the C-atoms (see B. 3)

2062).

Hydroïndol Derivatives: A hydro-derivative of indol itself is not known. How ever, when the alkyl indols are reduced with tin and hydrochloric acid, dihydrochentives have been produced. Thus, a-methyl indol (methyl ketol) yielded dihydromethyl CH₂ CH . CH₃, boiling at 227°. Its behavior differs greatly from that of the mother substance. In its properties it is closely allied to the alkylic anilines. In its relations to tetrahydroquinaldine, which contains the six-membered hydrogenized pyridine ring condensed with the benzene ring, it behaves like ethyl- to propylandize (v. like homology, B. 26, 1285). Silver sulphate oxidizes dihydromethyl ketol back to methyl ketol (B. 27, 827). Malonic ester and dihydromethyl ketol form a tricyclic condensation product (B. 26, 1298):

$$\begin{array}{c} \text{C}_{6}\text{H}_{4} \searrow_{\text{NH}}^{\text{CH}_{2}} \nearrow \text{CH} \text{. CH}_{3} + \underset{\text{ROOC}}{\overset{\text{ROOC}}{\text{POC}}} \nearrow \text{CH}_{2} & \longrightarrow \\ & \downarrow \\ \text{CH}_{2} & \longrightarrow \underset{\text{CO}}{\overset{\text{CH}_{3}}{\text{CO}}} \nearrow \text{CH} \text{. CH}_{p} \end{array}$$

which can also be regarded as a derivative of a diketotetrahydroquinoline (see this): a_*a_* Dimethyldihydroïndol, $C_6H_4 < {}_{NH}^{CH_3} > C : (CH_3)_2$, boiling at 210°, is readily

produced by distilling o-isopropylamidobenzyl alcohol, C₆H₄< CH₂, OH OH CH(CH₃);

Oxygen-containing Dihydroindol Derivatives. Dihydroketoindols or Indolinons have been prepared by the condensation of acidi methylphenylhydrazides by means of lime:

$$C_6H_5N(CH_3)NH \cdot CO \cdot CH(CH_3)_2 \xrightarrow{-NH_3} C_6H_4 < \frac{C(CH_3)_2}{N(CH_3)} > CO$$

n,β,β-Trimethyl Indolinon, melting at 50° (25°) and boiling at 265°, is formed rom isobutyrylmethylphenylhydrazide, and may also be prepared by oxidizing the base 11 H₁₈NO, resulting from the condensation of isobutylidenemethylphenylhydrazine with alcoholic zinc chloride, with an ammoniacal silver solution. Further, trimethylindolinon is also been produced by oxidizing the so-called trimethyldihydroquinoline from indol as also been produced it again yields the base C₁₁H₁₅NO, which is therefore probably Trimethyl-a-oxyindolin (compare C. 1897, II, 120). n,β-Dimethylindol-ison, C₄H₄[C₂HNO(CH₃)₂], melting at 23° and boiling at 273-277°, is formed from - Tropionylmethylphenylhydrazide (M. 17, 479).

The anhydrides or lactams of some of the o-amido-acids of benzene belong here. They have been previously described, but because of their intimate relationship to indol will be again brought together:

1. Lactam of o-amidophenylacetic acid. This is oxindol or α-ketodihydroïndol (β-ketodihydroïndol is the ψ -indoxyl which was just

_described above).

2. Lactam of o-amidomandelic acid. This is dioxindol or a-keto-β-oxyhydroïndol.

3. Lactam (or lactime) of o amidobenzoyl formic acid. This is isatin or a,β-diketohydroindol.

These compounds change readily into one another as a result of reduction or oxidation:

1. Oxindol, $C_0H_5NO = C_0H_4 < \frac{CH_2}{NH} > CO$. Its properties have been given on p.

224. It was first obtained by the reduction of dioxindol; and in a moist condition, on exposure to air readily reoxidizes to the latter. It therefore reduces an ammoniacal aliver solution. Nitrogen trioxide converts it into isatoxime (p. 472). By reduction the latter becomes amido-oxindol and this isatin by oxidation:

Di-oxindol, C₈H₄ CH(OH) CO. Its properties are given on p. 251. It is readily obtained by boiling isatin with zinc-dust and hydrochloric acid. It oxidizes readily in aqueous solution to isatid and isatin. It is also obtained by the reduction of isatigo.

258. The following methods for its formation may be especially mentioned:

I. The oxidation of indigo with nitric acid (Method of preparation, J. pr. Ch. [2], 24, 11; 25, 434).

2. The oxidation of oxindol and dioxindol.

3. The action of alkali upon o-nitrophenylpropiolic acid, when there occurs at first rearrangement into isatogenic acid, which then loses carbon dioxide and becomes statin:

$$C_6H_6 < \stackrel{C \equiv C \cdot COOH}{NO_9} \longrightarrow C_6H_6 < \stackrel{CO}{N} \stackrel{C.CO_9H}{O} \longrightarrow C_6H_6 < \stackrel{CO}{N} \stackrel{C(OH)}{N}$$
Witness boundaries letter and the Aside Asid

o-Nitrophenylpropiolic Acid

Isatogenic Acid

Isatin

If a reducing agent be added to the alkaline solution of the o-nitrophenylpropiolic acid, indigo will result instead of isatin (see below).

Behavior:

(1) Isatoic Acid, Cell (), is formed when isatin is exidized with chemically

in glacial acetic acid solution.

Isatin yields nitrosalicylic acid when oxidized with nitric acid. (2) When reduct with aumonium sulphide we get first isatid, C₁₆H₁₂N₂O₄, then dioxindol and oxidel.

(3) Ammonia and primary amines form Imesatins of the general formula

(3) Aminonia and primary amines form americans of the general formula $C_6 \Pi_4 < NH > CO$, which, when digested with alkalies, decompose again into intin ad

o-Phenylenediamine yields indophenasine (B. 29, 194, 1030); piperidine yields a diperidyl isatin, C_aH_aNO(NC_aH₁₀)₂, which can be converted into a dye—intia Massimilar to indigo (B. 24, 1366). (4) Isatin condenses, further, with benzene hydroxidon, phenols, etc. Water exit occurs. It forms with thiophene the blue dye indophenic (C_aH_bNO₂ + C_aH_aS — H_aO). Similar products are obtained with furfurane and pyrol. (5) The hydroxyl or lactime formula of isatin furnishes alkali salts; from the solution of the latter silver nitrate precipitates ailver isatin, C_aH_a(OAg)NO, with which also isating yield O-alkyl isatins: Methyl Isatin, C_aH_a(OCH_a)NO, melting at 104; Ethyl Isatin, C_aH_a(OC₂H_a)NO, melting at 88°, which can be resaponified to isatin at isatinates. (6) The keto-(lactam or pseudo-) form of isatin yields: n-Methyl-pisatin, C_aH_a: (C₂O₂N—CH₃), melting at 134°, and n-Ethyl-p-isatin, melting at 95°. These are obtained by the action of NaOBr upon n-methyl and n-ethyl indol (p. 467). The second companion is also formed from ethyl-p-isatin ethyloxime (see below). n-Actiply isatin, C_aH_a: (C₂O₂C. C₂H₃O) (p. 258), is obtained from isatin and acetic mhydrides.

Isatoxime, C_6H_4 C = NOH Normalis at 202°, with decomposition. It is prepared

from isatin and hydroxylamine; or from oxindol by action of nitrous acid, and when reduced it yields so called amido-oxindol, which can be oxidized to isatin. By the secessive action of ethyl iodide upon the silver salt we obtain a mono- and a diethyl derivative from which isatin (B. 16, 1706) is formed after saponification, which would indicate that the ethyl groups are combined with oxygen.

Pseudo-isatoxime, $C_6H_4 < \frac{CO}{NH} > C = N$. OH, melting with decomposition at 200³, is prepared by the action of nitrous acid upon ethyl indoxylic acid. Ethyl iodide converts it into (1) a mono- and (2) a diethyl derivative. The first alone yields isain, whereas the second is converted into n-methyl- ψ -isatin:

The reduction of n-ethyl- ψ -isatin-ethoxime produces n-diethyl indige (B. 16, 2201) A dioxime is formed by n-acetyl- ψ -isatin and hydroxylamine. See B. 29, 1030, for

8. Isatin Chloride, C₈H₈NO(: NNHCONH₂).

8. Isatin Chloride, C₈H₄CO CCI, melting with decomposition at 180°, is produced by digesting isatin with PCI, in benzene solution. It

180°, is produced by digesting isatin with PCl, in benzene solution. It dissolves with a blue color in ether. It is reduced in glacial acetic acid solution by hydriodic acid or by zinc-dust to *indigo-blue*:

$${}^{2C_{0}H_{4}}$$
 CO CCI $\xrightarrow{4H}$ $C_{0}H_{4}$ $CO.C:C.CO$ $C_{0}H_{4}$ $+$ $2HCI.$

We can also obtain from the isatins substituted in the benzene nucleus substitution products of indigo-blue: dibrom-, dinitro-, and dimethyl indigo-blue.

Indigo-blue (Indigotin), $C_6H_4 < {}^{CO}_{NH} > C = C < {}^{CO}_{NH} > C_6H_4$, constitutes the principal ingredient of commercial Indigo, derived from different Indigofera and from woad (Isatis tinctoria). It occurs in these plants as a glucoside, called indican, which parts with its variety of glucose and becomes indigo-blue, when boiled with dilute acids, or if acted upon with a ferment (if the various portions of the plant be covered with water and exposed to the action of the air). The indigo-blue separates in the form of a powder.

Commercial indigo contains, in addition to 20–90 per cent. of indigo-blue, various other substances, which have not been well studied, like indigo gluten, indigo-brown, and indigo-red, which are removed by successive treatment with dilute acetic acid, caustic potash, and hot alcohol.

A better procedure consists in first reducing indigo by means of grape-sugar and sodium hydroxide to soluble indigo-white, which can then be oxidized to indigo blue by the exposure of the alkaline solution to the air, when the indigo-blue will separate in a pure condition (A. 195, 305).

History: Indigo was in ancient times highly prized as a dye by the Oriental nations (Dioscorides, Pliny: 1νοίκον, indicum). In Europe it found general application in dyeing, from the opening up of sea-intercourse with the East Indies to he 16th century. To-day the production of indigo from plants, chiefly in Bengal, Java, Central America, is about \$300,000,000 kg., equivalent in money to about \$20,000,000.

In the period of the alchemists indigo was quite frequently considered in Europe as a mineral or metal (compare Schultz: Steinkohlentheer, 2 Aufig. II, 883), presumably because of its copper-like lustre. More careful investigations into its chemical nature were first instituted in this century. Erdmann and Laurent observed simultaneously (1841) that nitric acid oxidized indigo to isatin, while Fritzsche found (1848) that aniline sesulted when it was distilled with caustic potash. Baeyer and Knop (1865) reduced it to dioxindol, oxindol, and indol. The latter body Baeyer and Emerling (1869) obtained synthetically from o-nitrocinnamic acid, and when Nencki (1874) succeeded in oxidizing indol to indigo with ozone, the first synthesis of this interesting compound was achieved (compare, however, Engler, B. 28, 312). Baeyer and his students (1870–'78) demonstrated the constitution and synthesis of oxindol or o-amidophenyl acetic acid lactam, its conversion into isatin, as well as various methods for the conversion of isatin into indigo blue. Claisen and Shadwell (1879) also obtained isatin from o-amidobenzoyl formic acid. Baeyer (1880–'82), by a series of new syntheses of indigo, produced more certain evidence of its constitution and found easy methods for its production. These, and even later syntheses, have, however, not succeeded in fulfilling technical expectations.

Syntheses of Indigo-blue: Different methods of producing indigo have been presented in the preceding paragraphs. A particularly easy procedure is (1) the oxidation of *indoxyl* (p. 468) with ferric chloride and hydrochloric acid:

$$2C_{\theta}H_{4} \stackrel{C(\mathrm{OH})}{\nearrow} CH + 2O = C_{\theta}H_{4} \stackrel{CO}{\nearrow} C = C \stackrel{CO}{\nearrow} C_{\theta}H_{4} + 2H_{2}O,$$

as well as (2) the reduction of isatin chloride (p. 472):

Syntheses 3, 4, and 5 commence with o-nitrocinnamic acid, which can be prepare

in the following manner from the elements:

Acetylene, synthesized from carbon and hydrogen, polymerizes to benzene. Bron benzene with methyl iodide and sodium yields toluene, which chromyl chloride c something of that nature will convert into benzaldehyde. The latter is changed by acet anhydride and sodium acetate into cinnamic acid, which upon nitration is mainly change to o-nitrocinnamic acid:

3. Potassium permanganate oxidizes o-nitrocinnamic acid to o-nitro benzaldehyde, which condenses with acetone to o-nitrophenyl lactic acid methyl ketone. The alkalies decompose this ketone quite readily into acetic acid, water, and indigo-blue:

$${}^{2C_6H_4} < ^{CH(OH)\,.\,CH_2\,.\,CO\,.\,CH_3}_{NO_2} = C_8H_4 < ^{CO}_{NH} > C = C < ^{CO}_{NH} > C_8H_4 + 2CH_5COOH + 2H_2O.}_{O-Nitrophenyl \,Lactic \,Acid \, Ketone}$$

4. o-Nitrocinnamic acid is changed by means of the dibromide into o-nitrophenylpropiolic acid. Alkaline reducing agents cause a rearrangement to isatogenic acid, and then, by the elimination of carbon dioxide, produce indigo:

$$\begin{array}{c} C_{8}H_{4} \stackrel{\textstyle CC : C.COOH}{\textstyle C_{8}H_{4}} \stackrel{\textstyle CO > C.COOH}{\textstyle C_{8}H_{4}} \\ \hline \\ {}_{1Satogenic\ Acid} \\ {}_{2}C_{6}H_{4} \stackrel{\textstyle CO > C.COOH}{\textstyle C.COOH} \stackrel{\textstyle H}{\textstyle C_{8}H_{4}} \\ \hline \\ {}_{1Indigo-blue.} \\ \hline \end{array}$$

5. On the other hand, by exit of CO, from o-nitrophenylpropiolic acid, o-nitrophenyl acetylene is produced. Potassium ferricyanide condenses its copper derivative to di-(o-nitrophenyl)-diacetylene (p. 380), which alkalies rearrange to di-isatogen, and reducing agents change to indigo-blue:

The following indigo syntheses are very simple:

The following indigo syntheses are very simple:

6. Fusion of bromacetanilide, C₈H₅. NH. CO. CH₂Br, with caustic potash. The indoxyl formed at first is then oxidized by the air to indigo-blue (B. 23, 3289).

7. Indigo can also be formed by fusing phenylglycocoll, C₈H₅. NH. CH₂. CO₂H, with potassium hydroxide. Tolyl-, xylyl-, naphthyl-, phenylmethyl glycocoll, behave similarly and yield indigo-blue derivatives (B. 23, 3043, 3431; 24, R. 380; 25, R. 488; 26, 2547). Phenylmethyl- and phenylethyl glycocoll, when acted upon with fuming sulphuric acid (B. 26, R. 633), form their corresponding indigo-sulphonic acids.

8. The careful heating of o-nitroacetophenone, C₈H₄ < COCH₂, with zinc-dust yields a sublimate of indigo-blue (B. 28, 200).

a sublimate of indigo-blue (B. 28, 309).

iene-o-nitroacetophenone, $C_6H_4 < \frac{COCH : CH \cdot C_6H_8}{NO_2}$, readily breaks down influence of sunlight into indigo-blue and benzoic acid (B. 28, 2497). production of indigo when ethylene anthranilic acid, OH HOOC>C₆H₄, is fused with caustic potash belongs to this class **≅** (B. **28**, 1685).

itution of Indigo-blue: The formula adopted for indigo is on the following facts:

e vapor density corresponds to the molecular formula C18H10N2O2. e ready formation of indigo-blue from indoxyl and isatin, as well y conversion into these bodies and into other indol derivatives, ument in favor of the view that the indigo formula is produced nion of two groups, $C_6H_4 < \overset{\circ}{N} > C$:

at these two residues must be linked to each other by Cevidenced by the synthesis from di-(o-nitrophenyl)-diacetyl-: above), which would indicate that diphenyl diacetylene, $C-C: C. C_6H_6$, is the parent hydrocarbon of indigo (see p.

e formation of n-diethyl indigo from n-ethyl- ψ -isatin shows the of NH-groups (p. 472).

ties: Indigo-blue is a dark-blue powder with a reddish glimmer; es metallic and copper-like under pressure. It sublimes in copmetallic, shining prisms. It is insoluble in water, alcohol, and alkalies and dilute acids, and is odorless and tasteless. It dishot aniline with a blue, in molten paraffin with a purple-red, color portment recalls the various colors of iodine solutions), and can llized from these solvents. It crystallizes from hot oil of turpeneautiful blue plates. Heated at the ordinary pressure it partially ses and is converted into a dark-red vapor. The same occurs omposition under 30-40 mm. pressure. See B. 18, 1426, for the on spectrum of indigo and its derivatives.

wool) are dyed in two ways with indigo: (1) the wool is immersed in the lution of indigotin sulphonic acid, which fixes itself directly (Saxony-blue r (2) the indigo-blue is changed by fermentation to indigo-white (indigo-vat), aturated with the latter and exposed to the air, when indigo blue forms and apon the fibre. (3) In printing, a mixture of o-nitrophenylpropiolic acid and reducing agent are sometimes substituted for the indigo. Steaming causes the of indigo-blue.

zently the bisulphite derivative of o-nitrophenyl-lactic acid ketone has been used derable success as the indigo salt. When printed in mixture with alkali and

ed, it changes to indigo-blue.

ed, it changes to indigo-blue.

The of Indigo-blue: Dichlor-, dibrom-, dinitro-indigos, have been rom substituted isatins and o-nitroacetophenones (see methods of formation 2 Bz-3,5-Dimethyl Indigo, (CH₃)C₆H₃(C₄O₂N₂H₃)C₂H₃(CH₃), is formed from toluic aldehyde (compare method of formation 3, p. 471). n-Diethyl C₆H₆: C₇ON. C₇H₈), is produced from n-ethyl-\$\psi\$ isatin ethyloxime (p. 472).

3-Naphthyl Indigo, (C₁₀H₆: C₇ONH), are produced by melting together the mines with chloracetic acid and caustic potash and then oxidizing in according to the production of indigo-blue (R. 26, 2547). method 7 for the production of indigo-blue (B. 26, 2547).

has been digested for some time indigotin monosulphonic acid, placencin sulpha acid, C₂H₂N₂O₃. SO₂H₁, is produced. Water precipitates it from its solution in form of a blue powder. It forms salts with a pusple-sed color; these are soluble water. Indigotin Disulphonic Acid, C₂H₂N₂O₃(SO₂H)₂, is formed by the action funing sulphuric acid. It forms alkali salts which disastes with difficulty in salt so tions, and occur in trade as indigo carmine in paste form.

Indigo Dicarboxylic Acid, C₂H₂N₂O₃(COOH)₂, is obtained from o-nitrophth aldehydic acid, C₃H₃(COOH) In 1.35 lisses es in contrentrated sulphanic acid with a green color. After the solut

debyde.

Indigo-white, C_BH_BN₂O_B is obtained by the reduction of indig blue (see above). It can be precipitated from its alkaline solution l hydrochloric acid (air being excluded) as a white crystalline powde soluble in alcohol, ether, and the alkalies, with a yellowish color. As results from indigo by the absorption of two hydrogen atoms, and because of its phenol-like nature, it is ascribed the formula of a di-indexyl:

It rapidly re-oxidizes to indigo-blue by exposure to the air. It yield di-indol when heated with baryta-water and zinc-dust.

Indigo-red and indigo purpurin are isomerides of indigo-blue. The first occurs i commercial indigo, while the second is produced, together with indigo, from issti chloride.

Indirubin, the indogenide of pseudoissatin, and indin, formed from issatid by fusion with caustic potash, or from dioxindol, are identical with indige purpurin (B. 28, 540).

melting at 81° and boiling at 288°, occurs in small quantities in "stubb-fat," and may be obtained synthetically (1) by distilling phenyl phosphate (p. 147) with lime; (2) by the same treatment of phenol with lead oxide; (3) on conducting phenyl ether through tuber heated to redness; (4) by decomposing the diazo-derivative of o-amido-phenyl ether with sulphuric acid (compare p. 147 and B. 29, 1876); and best by the action of dilute acids upon the tetrazo-compound of o₂-diamido-diphenyl (p. 337) (B. 25, 2746):

$$C_eH_4 \xrightarrow{NH_3 NH_3} C_eH_4 \xrightarrow{N_5O_6} C_eH_4 \xrightarrow{O} C_eH_4$$

Bromine converts diphenylene oxide into dibromdiphenylene oxide, melting at 185°. Fuming nitric acid changes to dinitrodiphenylene oxide, melting at 200°. Diamidodiphenylene oxide, melting at 188°, yields valuable substantive azo-dyes (p. 338). Acetyldiphenylene oxide melts at 81°; see B. 24, R. 744.

CH/CH/CC—C/CH/CH

melting at 97° and boiling at 333°, is produced when phenyl disulphide, $(C_0H_0)_2S_3$, and phenyl sulphide, $(C_0H_0)_2S_3$, are distilled through tubes heated to redness. Chromic acid oxidizes it, in contradistinction to thiophene (p. 453), to diphenylene sulphone,

$$(C_0H_4)_0SO_1$$
, melting at 230°. Dinaphthylene Thiophene, S_0H_0 , melting

247°, is constituted analogously to dibenzothiophene. It results when concentrated sulphuric acid acts upon dioxydinaphthylene sulphide (B. 27, 3002).

zo. Dibenzopyrrol, Diphenyleneimide or Carbazole,

occurs in crude anthracene. It is withdrawn from it as carbazole-potassium by fusion

with caustic potash. It may be synthesized:

(1) By conducting diphenylamine through tubes heated to redness; (2) by heating thiodiphenylamine with copper in powder form; (3) by distilling o-amidodiphenyl with lime (B. 24, 306); (4) by heating o-diamidodiphenyl with acids (B. 25, 133); (5) from o-amidodiphenylamine through the diazo-compound. The phenylazimidobenzene, produced at first, yields, when exposed to a higher temperature, nitrogen and carbazole (A. 291, 16):

(2)
$$C_6H_6 \sim_{NH} \sim_{C_6H_4} \sim_{C_6H_4} \sim_{C_6H_4} \sim_{C_6H_4} \sim_{C_6H_4} \sim_{NH_2} \sim_{C_6H_4} \sim_{NH_2} \sim_{C_6H_4} \sim_{NH_2} \sim_{C_6H_4} \sim_{NH_2} \sim_{C_6H_4} \sim_{NH_2} \sim_{C_6H_4} \sim_{NH_2} \sim_{NH_2}$$

Behavior: Carbazole gives the pine-shaving reaction (p. 457) and the blue coloration with sulphuric acid and isatin (p. 453), just the same as the pyrrol and most of the indol derivatives. This and its other deportments would justify the conclusion that it is dibenzopyrrol or benzoIndol—e. g., tetrahydrocarbazole, when fused with potassium hydroxide, breaks down into a-indol carboxylic acid:

Carbazole, like pyrrol, is a very feeble base. It forms a stable salt with picric acid; the picrate melts at 182°. Nitrous acid converts it into nitrosocarbazole, $(C_6H_4)_2N$. NO, melting at 84°. Heated with potash it yields carbazole-potassium, $(C_6H_4)_2N$. Alkyl iodides convert this into n-methyl carbazole, (C_6H_4) N. CH₃, melting at 87°, and n-ethyl carbazole, $(C_6H_4)_2N$. CDCH₃, melting at 68°. Carbazole and acetic anhydride yield n-acetyl carbazole, $(C_6H_4)_2N$. COCH₃, melting at 69°. Chlorine produces various chlorcarbazoles, nitric acid, nitrocarbazoles (A. 202, 27; B. 29, R. 292, 650, 1112). See p. 338 for diamidocarbazole. When carbazol and oxalic acid are fused together Tricarbazole Carbinol or Carbazole Blue (compare p. 358) results. Dimethyl Carbazole, Ditolylimide, $(CH_3 \cdot C_6H_3)_2NH$, melting at 364°, is made from o-toluidine by the pyrogenic method (B. 29, 2594).

Hydrocarbasoles: Tetrahydrocarbazole, C6H, NII/C6H8, melting at 119°, re-

sults from the reduction of carbazole, as well as from the phenylhydrazone of ketohexamethylene, analogously to Fischer's indol synthesis (p. 296). It behaves like an alkylic indol (compare hydronaphthalenes, p. 466). When acted upon by alkyl iodides or with ethoroform, it passes in a similar manner into acridine derivatives, just as the indols become quinoline compounds (Gaz. chim. ital. 24, 111). By the potash fusion it, like the alkylic indols, yields indol carboxylic acid (see above and B. 26, 2006). Tetrahydrocarbazole Carboxylic Acid, ${}^{C_6H_4} \overline{\backslash_{NH}} {}^{C_6N_7}$. COOH, melting at 230°, is formed from the phenylhydrazone of ketohexahydrobenzoic acid (p. 301) (B. 22, 2185). Hexahydrocarbazole, ${}^{C_6H_4} \overline{\backslash_{NH}} {}^{C_6H_{10}}$, melting at 99° and boiling at 207°, is a strong base (A. 163, 352), just like the pyrrol and indol hydrides (pp. 461, 470).

The following are similar to carbazole in method of production and in their behavior: Phenylnaphthyl-carbazole or Naphthophenocarbazole, $C_8H_4 \sim NH$ $C_{10}H_6$ (B. 27, 3066), melting at 330°, occurs in coal-tar (B. 12, 2242). An isomeric naphthophenocarbazole, melting at 120°, is obtained by a zinc-dust distillation from its carbazole acid, C_8H_4 . NH . $C_{10}H_5$. COOH, melting at 335°, which results from the indol condensation of phenylhydrazine with 2,3-oxynaphthoic acid (p. 408). Dinaphthyl-carbazole or Dinaphtho-carbazole, $C_{10}H_6 \sim NH$ $C_{10}H_6$; the a-body melts at 216°, and the 3-coapound at 170° (B. 19, 2242).

B. POLYHETEROATOMIC FIVE-MEMBERED RINGS.

The acetals and mercaptals of ethylene glycol—e. g., ethylene-ethidene ether,

CH₂ = O
CH . CH₃, and ethylene dithioethidene, CH₂ = S
CH . CH₃ (1, 298, 305)—
are five membered rings with two O or S atoms. This is also the case with the ethylene esters
of the carbonic acid group—e. g., carbonic ethidene ester, CH₂ = O
CH₂ = O
CH₂ = S
CS (1, 202), the ethidene esters of governcists—t.

carbonic ethylene ester, $CH_2 - S$ CS (1, 392), the ethidene esters of a-oxyacids—e.g., $CH_2 - S$ CH = O CH = O

Several five-membered cyclic esters and amido-derivatives have also been obtained from phosphoric acid—e. g., the lactone of benzoylphenylhydrazido-phosphoric acid.

 $N = N(C_6H_5)$ POOII, which results on treating the reaction product of PCl₅ and Denzoylphenylhydrazine with methyl alcohol. o-Toluylene diamine and PCl₅ or PCl₅ yield compounds like $C_7H_6 < \frac{NH}{NH} > PO.NH.C_7H_6.NH_2$.

AZOLES.

There is another group, of greater importance than those discussed. It comprises the bodies containing polyheteroatomic five-membered rings, which are embraced under the name azoles (A. 249, 1; B. 24, 2824; B. 22, R. 737). They contain as hetero-atoms N and O, N and S, or only N-atoms. We may view them as derived from the monohetero-atomic rings—furfurane, thiophene, and pyrrol—by the replacement of methingroups by N-atoms, whereby, as previously indicated, the stability of the ring is very slightly affected. Viewing the numerous classes of bodies

AZOLES. 479

longing here as ring-azo-substitution products of the monoheteromic rings, we arrive at a natural systemization of the former, and also
sch a simple nomenclature for them, which in many instances is quite
nilar to the names which have become peculiar to the individual
sups. The individual azoles, depending upon whether they are
rived from furfurane, thiophene, or pyrrol, by the replacement of one,
o, or three CH-groups by N-atoms, are designated as furo-monazoles,
io-diazoles, pyrro-triazoles. To distinguish the metameric rings the
thine groups of furfurane, etc., are termed

[b]CH = CH[a] |, [a_1], [b], [b_1] | > R, and the substituents as a, a_1 , β , β_1 (p. $[b_1]$ CH = CH[a_1],

7), so that we distinguish furo-[a]-monazole, furo-[b]-monazole, pyrro-[a]-diazole, pyrro-[ab]-diazole, pyrro-[ab]-diazole, etc. Retaining the mes of the individual bodies and the groups introduced by their disverers, there will in the following page be placed at the beginning of ch individual group the names resulting from the introduction of the menclature just described. This will render the constitution and the sition of the azoles in the system, which follows, very evident:

CH = CH CH = CH Furfurane	CH = CH > S $CH = CH > S$	CH = CH > NH $CH = CH > NH$ $Pyrrol$
CH = N CH = CH Furo-[a]-monazole, Isoxazole (p. 493)	CH = N CH = CH Thio-[a]-monazole, Comp. Benzisothiazole (p. 597)	CH = N CH = CH Pyrro-[a]-monazole, Pyrazole (p. 480)
N = CH CH = CH Furo-(b)-monazole, Oxazoles (p. 502)	N == CH CH = CH Thio-[b]-monazole, Thiazoles (p. 504)	N — CII CH = CH Pyrro-[b]-monazole, Imidazoles, Glyoxalines (p. 496)
CH = N CH = N CH = N Furo-{aa ₁ }-diazole, Furazanes (p. 514)	CH = N $CH = N$ S $Chi = N$ S $Chi = N$ S	$CH = N$ $CH = N$ $Pyrro-[aa_1]-diazole,$ Osotriazole (p. 508)
N == N CH = CH >O Furo-{ab}-diazole, labydrides of o-Diazo- phenols (p. 516)	N == N CH = CH > S Thio-[ab]-diazole, Anilidothlobiazole, Phenylenediazosul- phides (p. 517)	N == N CH=CH>NH Pyrro-[ab]-diazole (p. 510)
N = CH N = CH Furo-[bb ₁]-diazole, Oxybiazoles (p. 516)	N = CH N = CH Thio-[bb]-diazole, Thiobiazolines (p. 517)	N=CH N=CH>NH Pyrro-[bb ₁]-diazole (p. 511)
N = CH CH = N Faro-[ab ₁]-diazole, Azozimes (p. 515)	N == CH CH = N Thio-[ab ₁]-diazole, Azosulphimes (p. 517)	N == CH CH == N > NH Pyrro-[ab ₁]-diazole, Triazoles (p. 511)

The parent substances of all the rings just given have not been prepared. In me instances, however, their next homologues are known; in some cases only the low derivatives. Only single representatives of the furo- and thiotriazoles are known at present time. It is, however, not impossible that by synthesis these rings, consist mainly of inorganic elements, may be multiplied and the system enlarged. Indeed, may succeed to such a degree that the purely inorganic rings—e.g., those constant from four N atoms and an NH-group—will be prepared. This would be a mention homologue of hydrazoic acid. From the standpoint of a nitrogen chemistry the Containing rings could be as readily evolved from the nitrogen ring by replacing the N-stat with CH groups, as was suggested above in the reverse case.

The numerous and important pyrazoles, together with their benzo-derivatives, theisd zol s, consisting of dihetero-atomic rings, will be next discussed; then will follow the benzo-derivatives, the indoxazenes. After this will appear the production of inidazoles, the oxazoles, and the thiazoles, sometimes in conjunction with the henzo derivatives, which it is customary to consider under the name of anhydroka (pp. 115, 1153, 1157), because they are formed from o-diamines, o-amidophenols, and o-amid thiophenols with carboxylic acids by the exit of water. In the trihetero atomic ingagin, the groups of the pyrrodiazoles or triazoles are placed first; the azimidate pendiazonidate belong to their benzo-derivatives. Attached to these are the fundamole the fundamoles, according to their benzo-derivatives. Attached to these are the fundamole the fundamoles, according to their benzo-derivatives, and the thiodiazoles: azonding this bidistriance, plantificate (plantinols), thio-[ab]-diazoles, and phenylenediazonification or the triazoles and tetrazoles conclude the list.

1. PYRAZOLE- OR PYRRO-[a]-MONAZOLE GROUP.

Pyrazole, $C_0H_4N_2$, may be regarded as derived from pyrrol by replace ment of a methine-group adjacent to an NH-group by nitrogen—firm [a]-monazole (see above). See 3-methylpyrazole (p. 482) for details it regard to the constitution of pyrazole. There are a dihydropyrazole pyrazoline and a tetrahydropyrazole or pyrazolidine corresponding to the di- and tetrahydropyrrols.

Keto-substitution products of these hydrogenized pyrazoles are kete pyrazoline or pyrazolen, among the derivatives of which is the febrifing antipyrine, ketopyrazolidine or pyrazolidone, and diketopyrazolidine, corresponding to the butyrolactam or pyrrolidone (p. 462) and succinimal The subjoined diagram indicates the relations existing between the pyrazole and the pyrrol derivatives:

^{*} The Parent substances, enclosed in brackets, are only known in their derivatives.

yrasole, C₃H₄N₃, melting at 70° and boiling at 187°, results from epichlorhydrin, azine hydrate, and zinc chloride (B. 23, 1105). A better method consists in splitaff CO₃ from its carboxylic acids (B. 26, R. 282), or in the action of bromine upon roline (p. 486) (B. 29, 775). It is a feeble base; its salts are unstable. It does not sine with methyl iodide. An ammoniacal silver solution precipitates pyrazole silver, H₂Ag, corresponding to pyrrol-potassium (p. 458). The platinum double salt, N₂. HCl₃PtCl₄, at 200-210°, loses four molecules of hydrochloric acid and best (C₃H₃N₃). PtCl₄ (B. 26, R. 185). n-Acetyl pyrazole, boiling at 156°, and sappl pyrazole, boiling at 281°, result from the action of acetyl chloride and benzoyl ide upon pyrazole (B. 28, 716).

be pyrazole derivatives are designated in the following manner:

I = N₂ NH I (or n); the numbering proceeds from the imide group, beyond the l = CH₃ and nitrogen atom.

Homologous Pyrazoles are formed:

From the hydrazones of the β -diketones and β -ketone aldehydes or oxymethylene ses. As a rule, the reactions proceed smoothly with the elimination of water, when retones are digested with the hydrazines:

by this procedure the unsymmetrical β -diketo-compounds yield two isomeric pyras; this is because the two possible hydrazones are formed. In the example cited the start is produced, together with 1,3,5-diphenylmethyl pyrazole. The oxalyl-RC = CH - C - CH = CR

N	N	N	C	CH	CR
N	N	C	CH	CR	
N	N	C	CH	CR	
N	N	C	CH	CR	
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH			
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	C	CH	CR		
N	CR	CR			
N	CR				

By the elimination of carbon dioxide from the homologous pyrazole carboxylic s (p. 484).

▶ By the exit of hydrogen from the pyrazolines (p. 485). Frequently, in reactions repyrazolines may well be expected pyrazoles appear. This is true of the interaction he hydrazines and epichlorhydrin:

Pyrazoles also result upon distilling pyrazolons or pyrazolidones with zinc-dust or

$$\begin{array}{c} \text{CH}_{3}\text{--CO} \\ \text{CH}_{3}\text{--}\text{CO} \\ \text{CH}_{5}\text{--}\text{C} \\ \text{Phenylmethylpyrazolon} \end{array} \xrightarrow{P_{2}S_{5}} \begin{array}{c} \text{CH} = \text{CH} \\ \text{CH}_{3}\text{--}\text{C} \\ \text{CH}_{3}\text{--}\text{C} \\ \text{Phenylmethylpyrazole.} \end{array} \xrightarrow{NC_{6}H_{5}}$$

. Certain hydrazones of mono-ketones yield pyrazoles when they are heated with lanhydrides (Bull. Soc. Chim. [3], 11, 115; see B. 28, 703 Anm. 4):

$$\begin{tabular}{ll} $^{\bullet}_{S}$.$ $C=N-NHC_{0}H_{5}$ \\ CH_{3} \\$$

Behavior: The homologous pyrazoles may be arranged in three groups: (1) pyras with free imide-group; (2) n-alkyl substituted pyrazoles, which can be obtained from the first class (or their silver salts) by the action of alkyl iodides—best by the distillation of the iod-alkylates (B. 28, 716) with an excess of alkyl iodide—or from β -diketones an alkylhydrazines; (3) n-phenyl substituted pyrazoles, which are made through the phenylhydrazines, and are chiefly distinguished by their stability and power of crystalization.

All pyrazole homologues are feeble bases. They form double salts with silver nitrat mercuric chloride, and platinic chloride. The platinum double salts, like pyrazole itsel part with 4 HCl on heating and become R₂PtCl₂ (R = the pyrazole residue). The usually combine with alkyl iodide to form ammonium compounds (see above).

Potassium permanganate oxidizes the c-alkylized pyrazoles to pyrazole carboxyli acids, in contradistinction to the pyrrols, which are burnt up by this reagent (B. 22 172).

In the n-phenylated pyrazoles during the oxidation the phenyl group is often split of and replaced by hydrogen. This is particularly true if it be amidated. The behavior is quite different during reduction. Pyrazoles with the free imide-group are but slightly altered by the reducing agents (A. 273, 266). n-Phenylpyrazoles are reduced to pyrazolines (p. 485), which yield intense colorations with ferric chloride, chromates, etc. (Knorr's pyrazoline reaction). In more energetic reductions trimethylene diaminal derivatives are formed by the rupture of the union between the N-members. In some n-phenylpyrazoles the reduction is accompanied by the splitting-off of the phenyl group as benzene or some similar group.

(1) Pyrazoles with free imide hydrogen: 3- (or 5-) Methyl Pyrazole,

- (1) from the interaction of oxymethylene acetone and hydrazine;
- (2) from its carboxylic acids;

(3) as well from 1,3. as from 1,5-phenylmethylpyrazole by elimination of the phenyl group through oxidation (A. 279, 217-225).

The last two methods show conclusively that 3-methyl pyrazole and 5-methyl pyrazole are identical. It is concluded, therefore, that pyrazole, like benzene, possesses "oscillating linkages"; the imide hydrogen atom is capable of oscillating between the two N-atoms (Knorr, A. 279, 188). The formula presented above for pyrazole is supposed

N-atoms (Knorr, A. 279, 188). The formula presented above for pyrazole is supposed to represent this condition.

3,5 Dimethyl Pyrazole, NH—N=C(CH₃)—CH=C(CH₃), melts at 107° and

boils at 220°. It is obtained from acetyl acetone and hydrazine, and from 1,3.5-phenyl-dimethyl pyrazole by reduction (elimination of the C₆H₅:group) (B. 25, R. 163, 744).

3,4,5-Trimethyl Pyrazole, $NH - N = C(CH_3) - C(CH_3) = C(CH_3)$, melting at 138° and boiling at 233°, is obtained from methylacetyl acetone. 3,4,4,5-Tetramethyl

Pyrazole, $N = C(CH_3) - C(CH_3)_2 - C(CH_3) = N$, melting at 50-55°, and boiling at 243°, is formed from dimethylacetyl acetone (A. 279, 244, 247). 3- (or 5-) Phenyl-

pyrazole, C₆H₅C = N -- N melting at 78°, is formed from benzoyl acetaldehyde (p. 250) (B. 28, 696).

Isomeric 4-Phenyl Pyrazole, melting at 228°, is obtained from 1,4-phenyl pyrazole carboxylic acid (A. 279, 254; B. 27, 3247; 28, 223, 699). 3,5-Phenyl Methyl

Pyrazole, $NH - N = C(CH_3) - CH = C(C_6H_5)$, melting at 128° and boiling at 317°, has been prepared from benzoyl acetone (A. 279, 248), as well as from phenylmethylisoxegule (p. 104), on besting with elsebelia appropria (B. 28, 2012)

isoxazole (p. 494), on heating with alcoholic ammonia (B. 28, 2952).

(2) n-Alkyl Pyrazoles: n- (or 1-) Methyl Pyrazole, C₄H₃N₂. CH₃, boiling at 127°, is formed in the interaction of pyrazole silver and methyl iodide (B. 26, R. 281; 28, 716).

1.3-Dimethyl Pyrazole, C₃H₂(CH₃)N₂. CH₃, boils at 150° (A. 279, 231); 1.3,5-Trimethyl Pyrazole, C₃H₃(CH₃)₁N₃CH₃, melting at 37° and boiling at 170°, crystallizes in combination with one molecule of chloroform.

1.3,4,5-Tetramethyl

Pyrazole, C₂(CH₂)₂N₂CH₃, boils at 190-193°. These compounds are also formed from acetyl acetone and methylacetyl acetone by the action of methylhydrazine (A. 279, 232, 235).

(3) n-Phenyl Pyrazoles: n- (or I-) Phenyl Pyrazole, C₃H₃N₃. C₆H₅, melting at II° and boiling at 246°, with sp. gr. I. II25, is obtained from epichlorhydrin and phenylhydrazine (see above), as well as from its carboxylic acids. It yields, upon reduction, phenylpyrazoline together with trimethylenephenyldiamine. n-Tolylpyrazole, C₂H₃. N₃. C₄H₇, melting at 33° and boiling at 259°, yields in like manner trimethylenetolyldiamine (Gaz. ch. ital. 18, 354). 1-Phenyl-3-methyl Pyrazole melts at 37° and boils at 255°. Its industrylate melts at 144°. The first body is derived from phenylmethylpyrazolon (p. 481, A. 238, 203; B. 24, 648), as well as from oxymethylene acetone together with the isomeric I-Phenyl-5-methyl Pyrazole,

 $C_0H_0\dot{N}-N=CH-CH=\dot{C}(CH_0)$. This is an oil, boiling at 255°. Its iodmethylate melts with decomposition at 296°. 1-Phenyl-4-methyl Pyrazole,

 $C_aH_a\dot{N} - N = CH - C(CH_a) = CH$, boiling at 266°, is formed by a rearrangement of the iodmethylate of 1-phenyl pyrazole (B. 26, R. 327). 1-Phenyl-3,5-dimethyl Pyrazole, C₄(CH₃)₂HN₃. C₆H₄, boiling at 273°, is obtained from acetyl acetone. Upon reduction it yields dimethyl pyrazole and benzene, together with 1-Tetrahydrophenyl-3.5dimethyl pyrasole, which, by oxidation, is decomposed into dimethyl pyrazole and adipic acid (B. 26, R. 246). 1-Phenyl-3,4-dimethyl Pyrazole, boiling at 278°, results from oxymethylene methylethyl ketone, CHOH = C(CH₂) — CO . CH₃ (B. 25, R. 943). 1,3-Diphenyl Pyrazole, C₂H₃(C₄H₅)N₂. C₆H₅, melting at 56° and boiling at 337°, is obtained from benzoylacetaldehyde (B. 21, 1135); 1,5-Diphenyl Pyrazole, melting at 54° and boiling at 340°, is derived from its carboxylic acid (B. 25, 3145); 1,3,5-Triphenyl Pyrazole, C₃H(C₆H₅)₂. N₂. C₆H₅, melting at 212°, is made from its carboxylic acid (B. 26, 1881). See A. 289, 332, for the production of 1,3,4-triphenyl pyrazole, melting at 185°, by the decomposition of 1,3,4,6-tetraphenyldihydropyridazine.

2. Haloid-, nitro-, amido-pyrazoles, pyrazole-sulphonic acids.—The halogens replace the hydrogen atoms in pyrazole. Bromine reacts most readily. The halogen atoms in the 4-position are most securely combined. In the sulphonation and nitration of pyrazole the NO, and SO, H-groups also enter the nucleus. n-Phenylated pyrazoles are nitrated and sulphonated in the phenyl residue. n-Sulphophenyl-pyrazole acids have also been prepared by the introduction of phenylhydrazine sulphonic acids in the pyrazole syntheses (A. 278, 296). In the nitropyrazoles the basic character of the pyrazoles dis-

appears. They are acids, which form stable sodium, potassium, etc., salts.

The amido-pyrazoles result in the reduction of the corresponding nitro-bodies. resemble the aromatic amines in their deportment. They have also been obtained by the action of hydrazines upon the nitriles of β -ketone-carboxylic acids and upon malono-

4-Brom-pyrazole, C₃H₃BrN₂, melts at 97°. 3-Methyl-brom-pyrazole melts at 67° (A. 279, 227). 1,3,5-Triphenyl-brom-pyrazole melts at 142°. 1-Phenyltribrom-pyrazole melts at 107°. Iod-pyrazole melts at 108° (B. 26, R. 281). 4-Nitro-pyrazole, C₂H₃(NO₂)N₂, melts at 142°. 3-Methyl-4-nitro-pyrazole, melting at 134° and boiling at 325°, is made by nitrating methyl-pyrazole or 3-methyl-5-pyrazole carboxylic acid with a mixture of nitric and sulphuric acids (A. 279, 228). 4-Nitro-1,3,5-trimethyl-pyrazole, melting at 57°, yields upon reduction:

4-Amido-1,3,5-trimethyl-pyrazole, melting at 103°, which may be readily converted into diazo-compounds, and subsequently, by combination with anilines, phenols, etc., into azo-dyes. 1-Phenyl-3,4-ethylmethyl-5-amido-pyrazole, melting at 81°, is prepared from methyl propionyl-acetonitrile, C₁H₂COCH(CH₃)CN, and phenylhydrazine (Bull. Soc. Ch. [4], 4, 647). 3,5-Diamido-pyrazole, C₃(NH₂)₂H₃N₂ (?), is formed from maloaonitrile and hydrazine acetate (B. 27, 690).

Methyl-pyrazole-sulphonic Acid, C₃H₃N₃(CH₃)(SO₃H), melting at 258°, is

formed when fuming sulphuric acid acts upon methyl-pyrazole (A. 279, 230).

3. Oxypyrazoles: In certain reactions the pyrazolons (p. 486) behave as such. alkylizing, these yield alkoxypyrazoles, together with isomeric n-alkyl derivatives (antipyrines). Further, compounds are also formed in the interaction of acid halvids and pyrazolons, which are probably to be viewed as esters of oxypyrazoles. The alkyl iodides and alkoxypyrazoles yield addition products, which also result from the antipyrines and alkyl iodides, and when they are gently heated, alone or with alkali, they are reconverted into antipyrines. The acid esters of the oxypyrazoles also yield alkyl iodide addition products, which may be resolved into antipyrines [J. pr. Ch. [2], 54, 177; 55, 145; A. 293, 42). Alkoxypyrazoles are also produced by the elimination of water from the hydrazones of the β -ketonic esters by means of suitable reagents.

n-Phenyl-5-ethoxy-pyrazole, $C_6H_5\dot{N}$. N: CH. CH: $\dot{C}(OC_2H_5)$, is formed from its carboxylic ester, which is produced by the condensing action of zinc chloride upon the phenylhydrazone of oxalacetic ester, then saponifying and splitting off carbon dioxide (B. 26, R. 550).

(B. 26, Ř. 550).

When the ethoxy-group is saponified with hydrochloric acid n-phenlypyrazolon, melting at 118° (p. 488; B. 27, 407), results. n-Phenyl-3-methyl-5-methoxypyrazole,

C₆H₅N. N: C(CH₃). CII: C(OCH₃), boiling at 240°, is formed when diazomethane acts upon phenyl-methyl-pyrazolon (B. 28, 1626), or methyl iodide and sodium methylate, together with the isomeric antipyrine (p. 488); also by the action of phenylhydrazine and hydrochloric acid upon the methyl ester of acetoacetic acid. Its iodmethylate, which is also produced from antipyrine and methyl iodide, readily changes to antipyrine on boiling with sodium hydroxide (p. 488 and A. 293, 17). n-Phenyl-3-methyl-5-ethoxypyrazole, melting at 38° and boiling at 301°, is formed from the phenylhydrazone of acetoacetic ester by means of acetyl chloride or an excess of hydrochloric acid. It into phenylmethylpyrazolon when it is saponified. Sodium and alcohol convert it into phenylmethylpyrazoline (B. 28, 627, 635, 706). The last two esters have also been obtained, by carbon dioxide elimination, from carbomethoxy- and carboethoxy-phenylmethylpyrazolons, products resulting from the action of chlorcarbonic methyl and ethyl esters upon phenylmethylpyrazolon (see above, and J. pr. Ch. [2], 54, 180; 55, 140).

4. Pyrazole Ketones are produced, like the thiophene, pyrrol, and indol ketones,

on heating the pyrazoles with acid chlorides:

1-Phenyl-4-acetyl-pyrazole, $C_3(\text{COCH}_3)\text{H}_3\text{N}_2$. $C_6\text{H}_5$, melting at 122°. Its oxime melts at 130° and its phenylhydrazone at 143° with decomposition. 1-Phenylbenzoyl-pyrazole, $C_3(\text{COC}_6\text{H}_5)\text{H}_2\text{N}_1\text{C}_6\text{H}_5$, melts at 123°; its oxime at 143° and its phenylhydrazone at 139° with decomposition.

5. Pyrazole Carboxylic Acids are produced

1. By oxidizing alkyl pyrazoles with potassium permanganate. When several alkyl groups are present they are gradually changed to carboxyl.

2. Pyrazole carboxylic esters are formed synthetically by the action of hydrazines upon the carboxylic esters of β -diketones or oxymethylene ketones:

C₆H₅CO.CH₂.CO.CO₂R + NH₂.NHC₆H₅
$$\rightarrow$$
 C₆H₅N-N = C(C₆H₅)-CH = C.CO₂R

Acetophenone Oxalic Ester

1,3-Diphenyl-5-pyrazole Carboxylic Ester.

The γ -diketonic esters also, which result from the interaction of bromacetone, bromacetophenone, etc., with sodium acetoacetic ester, yield, by action of diazobenzene salts with the splitting-off of the acetyl group, phenylhydrazones of β -diketone carboxylic esters, which condense to pyrazole carboxylic esters (B. 26, 1881).

3. Pyrazole carboxylic esters are formed by the addition of diazoacetic esters to monoand dicarboxylic acids of the acetylene series (B. 22, 2165; A. 273, 222);

Monohalogen substitution products of the acrylic and fumaric series and a,β -dihaloid architected saturated acids—e.g., a,β -dibrompropionic acid, dibromsuccinic acid, etc.—
thact with diazoacetic ester. When the pyrazole carboxylic acids are heated carbon disside is evolved and pyrazole results. The carboxyl group in the 3-position is most family split off. The next in order is that in the 5-position, while the COOH-group in the specifion is most family combined (A. 278, 273). There is no N-atom adjacent to it.

3- (or 5-) Pyrazole Carboxylic Acid, C₂H₂N₂. COOH, melting at 200° with decomposition is obtained from 2-mathyl processed (a. 200°).

3- (or 5-) Pyrazole Carboxylic Acid, $C_1H_1N_2$. COOII, melting at 200° with decomposition, is obtained from 3-methyl pyrazole (p. 482), as well as from 3,5-pyrazoline dicarboxylic acid by the exit of carbon dioxide and H_1 (A. 273, 237). 4-Pyrazole Carboxylic Acid, melting at 275°, is obtained from pyrazole tricarboxylic acid. 3,5-pyrazole Dicarboxylic Acid, $C_1H_1N_2$ (COOH), melting at 289°, is made from methyl pyrazole carboxylic acid, dimethyl pyrazole (A. 279, 218; B. 25, R. 744), as well as from diazoacetic ester by means of dibrompropionic ester. 3,4,5-Pyrazole Tricarboxylic Acid, C_2HN_2 (COOH), melting at 233°, is prepared by methods I and 3 (p. 484).

3-Methyl-5-pyrazole Carboxylic Acid, $C_2H_3(CH_3)N_2$. COOH, melts at 236° (B. 25, R. 744; A. 279, 217). 3,5-Dimethyl-4-pyrazole Carboxylic Acid, $C_2H_1(CH_3)_1N_2$. COOH, melting with decomposition at 290°, is derived from acetyl- or ethidene-aceto-acetic ester (A. 279, 239). Two isomeric c-Phenylpyrazole Dicarboxylic Acids, $C_2(C_2H_3)HN_2(CO_3H)_2$, melting at 235° and 243°, have been obtained from diazoacetic ester by means of phenylpropiol- and a-bromeinnamic acid (B. 27, 3247). n-Phenylpyrazole Carboxylic Acid, $C_2H_2N_2(C_2H_3)COOH$; the 3-acid melts at 146°, and the 5-acid melts at 183° (B. 24, 1888). The 4-acid melts at 220°. It is obtained from a-phenylpyrazole tricarboxylic acid (B. 22, 179). n-Phenylmethylpyrazole Carboxylic Acids, $C_3H_1(CH_3)N_2$. $C_3H_5(COOH)$. There are five known isomerides: (1) the 1,5,3-acid, melting at 136°, results from the action of diazobenzene chloride upon acetonyl acetoacetic ester (p. 484, method 2), as well as from acetone oxalic ester and phenylhydrazine, together with (2) the 1,3,5-acid, melting at 190°, which is also produced by a peculiar rearrangement of phenylmethyloxypyridazone (see this) (A. 253, 54; 295, 305); (3) the 1,5,4-acid, melting at 166°, is obtained from oxymethylene acetoacetic ester (A. 278, 270; 295, 311); (4) the 1,4,3-acid, melting at 134°, and (5) the 1,3,4-acid, melting at 192°, have been prepared by a half-sided oxidation of phenyldimethylpyrasole (B. 25, R. 943; 26, R. 245). 1,5-Diphenyl-3-pyrazole Carboxylic Acid, $C_4H_5(N_2, C_4H_5(COOH)_3$, melting at 185°, is prepared from phenacylacetoacetic ester; phenylpyrazole dicarboxylic acids—compare A. 295, 306. 1-Phenyl-3,4,5-tricarboxylic Acid, $C_4H_5(COOH)_3$, melts at 184° (B. 22, 172).

PYRAZOLINES.

Metallic sodium and alcohol reduce the pyrazoles, especially the n-phenylpyrazoles, to dihydropyrazoles or pyrazolines. The latter are also produced by rearrangement of the hydrazones of unsaturated aldehydes or ketones, in that the amine residue of the hydrazine adds itself to the unsaturated linkage:

$$\begin{array}{c|cccc} CH_2 = CH - CH & CH_2 - CH_3 - CH \\ \hline C_6H_5NH - N & C_6H_5N - N \\ \hline Acrolein Phenylhydrazone & n-Phenylpyrazoline. \end{array}$$

While this rearrangement proceeds with many hydrazones at lower temperatures, with others it is only completed when they are distilled. Frequently it occurs that the corresponding pyrazole (p. 481) is formed instead of the pyrazoline, or is produced along with the latter.

The ketazine of acetone, bisdimethylazimethylene, is capable of a rearrangement similar to the preceding. It is changed quite readily by maleic acid into maleinate of trimethylpyrazoline:

$$\begin{array}{cccc} CH_3-C=N-N & CH_3-C=N-NH \\ & CH_3 & C(CH_3)_2 & CH_3-C(CH_3)_3 \\ \text{Bisdimethylazimethylene} & 3.5.5-Trimethylpyrazoline.} \end{array}$$

Behavior: The pyrazolines are feeble bases. They are, for the most part, only soluble in concentrated acids. They are less stable than the pyrazoles. Oxidizing agents convert them into very unstable dye-substances, which are probably derived from bispyrazolines (B. 26, 100; Knorr's pyrazoline reaction). When reduced they frequently yield trimethylene diamine derivatives; this is particularly true of the n-phenylpyra-

Pyrazoline, $C_2H_6N_2=CH_1$ — CH_2 —CH=N-NH, is an oil, boiling at 144°. It is formed from acrolein and hydrazine hydrate (B. 28, 69; 29, 774). 3,5,5-Trimethyl-pyrazoline, $C_2H_3(CH_3)_3N_3$, boiling at 66-69° (20 mm.), is obtained from mesityl oxide and hydrazine, as well as from bis-dimethylazimethylene (see above); its picrate melis at 138° and its maleinate at 127° (B. 27, 770). 5-Phenylpyrazoline, $C_2H_5(C_6H_3)N_1$, is obtained from the hydrazone of cinnamic aldehyde (B. 27, 788), as well as from its dicarboxylic acid (B. 26, 261). n-Phenylpyrazoline, $C_2H_6N_2$. C_6H_6 , melting at 52° and boiling at 274°, is converted by bromine into n-phenyldibrompyrazoline, $C_2H_8Br_2N_2$. C_6H_6 , melting at 30° melting at 39°.

1,3,5. Triphenyl-pyrazoline, $C_3II_3(C_4H_5)_3N_3$, melting at 135°, is changed by bromine to triphenyltribrompyrazoline, $C_3(C_4H_5)_3Br_3N_3$, melting at 179°.

Pyrazoline carboxylic acids are obtained from diazoacetic ester or diazomethane by

means of olefine mono- and -dicarboxylic acids or mono-haloid saturated acids (compare p. 484):

The pyrazoline carboxylic acids show the rather remarkable peculiarity that when they are heated alone they break down into nitrogen and trimethylene carboxylic acids (p. 22). Hydra/ine is split off when they are heated with hydrochloric acid. Upon oxidation they become pyrazole carboxylic acids; and when their silver salts are heated, pyrazoles are produced. Upon reduction they yield pyrazoline compounds in part (p. 490) (E. Buchner, A. 273, 214).

Pyrazoline-3,5-dicarboxylic Acid, $C_3H_4N_9(COOH)_2$, melts with decomposition at 242°. Pyrazoline-4,5-dicarboxylic ester (B. 27, 1890), pyrazoline-3,4,5-tricarboxylic methyl ester, $C_3H_3N_3(COOCH_3)_3$, melting at 61°, and pyrazoline-3,4,5,5-tricarbonacetic trimethyl ester, $C_3H_3N_2(CO_2CH_3)_3(CH_3, CO_3CH_3)$, melting at 105°, are obtained from diazoacetic ester by means of fumaric and aconitic esters, while 5-Phenyl-3,4-pyrazoline Dicarboxylic Methyl Ester(?), C3H3(CaH5)N2(COOCH3), is formed from cinnamic ester and diazoacetic ester.

PYRAZOLONS.

The pyrazolons or ketodihydropyrazoles are those pyrazole derivatives which have been known for the longest time. They were discovered in 1883 and investigated by L. Knorr. Different pyrazolons have been previously discussed at the conclusion of the hydrazones of the β -ketonic acids, of which they are the inner anhydrides, and to which they sustain the same relation as the lactams bear to the corresponding amido-acids.

hence the designation lactazams was suggested for the pyrazolons (1,

They are produced (1) by the elimination of alcohol from the hydrazones of β -ketonic esters:

Phenylhydrazone-acetoacetic Ester

A number of these hydrazones when acted upon with condensing agents which eliminate water—e. g., hydrochloric acid, acetyl chloride, etc.—yield alkoxypyrazoles (p. 483), which subsequently are converted by saponification of the alkoxy-group into pyrazolons. Some of the phenylhydrazones of the β -ketonic esters, when treated with concentrated sulphuric acid, yield indol derivatives.

When hydrazines are condensed with the esters of β β -dilectone discrete varies of the property of the

e. g., diaceto-succinic ester and oxaldiacetic ester—bispyrazolons are produced (B. 28, 68): When hydrazines are condensed with the esters of β , β -diketone dicarboxylic acids—

$$\begin{array}{c} \text{CO-CH}_2\text{--C-CH}_1\text{. CO} \\ \text{J} & \text{I} & \text{I} \\ \text{N}(C_6H_6) - \text{N} & \text{N---N}(C_6H_6) \\ \text{Bisphenylpyrazolon} \end{array} \quad \begin{array}{c} \text{and} \\ \text{J} & \text{J} & \text{C}(\text{CH}_2)\text{C}(\text{CH}_3) = \text{N} \\ \text{Bisphenylmethylpyrazolon}. \end{array}$$

(2) By the oxidation of the corresponding pyrazolidones.

Behavior: The pyrazolons, like the other pyrazole derivatives, are feeble bases (see, however, antipyrine). They also manifest the acid properties of the β -ketonic esters, and therefore yield unstable salts with bases just as they do with acids. They also have a series of reactions in common with the derivatives of β -ketonic acids. This is due to the reactivity of the CH_s-group standing between the two CO-groups; they condense to bensylidene derivatives with bensaldehyde, and with nitrous acid form isonitroso- or witroso-compounds, while with diazobenzene salts they yield more or less intensely colored ass-compounds, etc. (B. 27, 782; 28, 625).

Different formulas have been proposed to show the constitution of the pyrazolons:

I.
$$N = CH - CH_2$$
II. $NH - CH = CH$
III. $NH - CH = CH$
 $NH - CH = CH$

Two isomeric n-phenylpyrazoles, corresponding to the formulas I and II, have been made in various ways. Furthermore, formula II corresponds to antipyrine, the most important member of the group (p. 488). It is, however, very often quite difficult to arrive at a distinction between the different possible formulas. The alkoxypyrazoles are derived from the hydroxyl form (III) of the pyrazolons. It is true that they are also produced from pyrazolons by various alkylization methods, together with the isomeric n-alkyl derivatives constituted according to formula II (B. 28, 706, 1626). The reaction products of acid chlorides and pyrazolons are also probably derived from the same formula (pp. 483, 484).

Pyrazolon, CO. CH2. CH: N. NH, melting at 164°, is best prepared from formyl-. acetic ester (1, 364) and hydrazine, but is also produced from its carboxylic acids. It condenses with benzaldehyde, nitrous acid, and diazobenzene chloride to 4-Benzal-pyrazolon, (C₂H₂ON₂): CHC₆H₅, melting at 200°, 4-isonitrosopyrazolon, (C₂H₂ON): NOH, melting with decomposition at 181°, and 4-pyrazolon-azobenzene, (C₂H₂ON): N. NHC₈H₅, melting at 196° (B. 29, 249).

3-Methyl Pyrazolon, C₃(CH₂)H₃ON₃, melting at 215°, is obtained by the action of hydrazine upon acetoacetic ester or dehydracetic ester (J. pr. Ch. [2], 39, 132).

n-Phenyl-5-pyrazolon, CO. CH₂. CH: N. N. C₆H₅, melting at 118°, is obtained both from n-phenyl-3- and 4-pyrazolon carboxylic acids and from 1-phenyl-5-pyrazoli-

done. n-Phenyl-3-pyrazolon, CH: CH. CO. NH. NC_aH₅, melting at 154°, result upon oxidizing 1-phenyl-3-pyrazolidone with ferric chloride, and by treating n-phenyl pyrazoline successively with bromine and caustic potash, etc. (B. 28, 35, 630; 29, 519 J. pr. Ch. [2], 52, 138).

n-Phenyl-3-methyl Pyrazolon, CO. CH_2 . $C(CH_3)$: N. NC_6H_6 , melting at 127° from acetoacetic ester, the β -chlorcrotonic esters (B. 29, 1654), or tetrolic acid by mean of phenylhydrazine, is that pyrazole derivative which is the best known, and indeed he been known for the longest time (A. 238, 147). With benzaldehyde it yields the hemph

dene compound, CO. C(: CHC₆H₆)C(CH₈): N. N. C₆H₅, melting at 107°; with N₂O₄

an isonitroso-derivative, CO. C(NOH)C(CH₂): N. NC₂H₂, melting at 157°, which may be oxidized and reduced to nitro- and amido-phenylmethyl pyrasolom. The latter is also made by the reduction of phenylmethyl pyrasolom associates. When the amido-derivative is oxidized it becomes rubasonic acid, C₂₂H₁₇N₂O₂, melting at 181°. It is a red-colored compound, which in its behavior recalls the purpuric acid (1, 510) of the aric acid group. A large excess of the oxidant converts amidopyrasolon immediately into

4-Keto-I-phenyl-3-methyl-pyrazolon, CO. CO. C(CH₃): N. NC₆H₅, the isatin of the pyrazole group, which, by reduction, yields the corresponding secondary alcohol:

4-Oxy-I-phenyl-3-methyl pyrazolon (A. 202. 50).

4-Oxy-1-phenyl-3-methyl pyrazolon (A. 293, 50).

Ferric chloride oxidizes phenylmethyl pyrazolon, with the union of two molecules, to

Pyrazole Blue,

Call Call Call Call A. Which resembles indigo-blue

in constitution and chemical behavior. Less energetic oxidants—e. g., phenylhydrasine, etc.—produce bisphenylmethylpyrasolom, which contains two atoms more of hydrogen. This can also be prepared from phenylmethylpyrasolon silver and iodine, as well as from the diphenylhydrazone of diacetosuccinic ester (p. 473). The interaction of diacetosuccinic ester (p. 473). The interaction of diacetosuccinic ester (p. 473). The interaction of diacetosuccinic ester (p. 473).

Antipyrine, 1,2,3-Phenyldimethyl Pyrazolon, CH₃N—CO—CH CH₃N—CCH₃ melting at 114°, is obtained in the form of its hydroiodide when phenylmethylpyrazolon is heated to 100°, together with methyl iodide and methyl alcohol. It also results by the condensation of symmetrical methylphenylhydrazine with acetoacetic ester (A. 238, 160; B. 20, R. 609):

$$C_6H_5.NH$$
 + $RO.CO.CH_5$ = C_6H_5N — CO — CH CO.CH₅ = C_6H_5N — CO — CH

Homologues of antipyrine are formed, similarly to it, from phenylmethylpyrazolon: -2 Benzyl- and 2-Ethyl-1-phenyl-3-methylpyrazolon, homoantipyrine, melting at 119° and 73° respectively (J. pr. Ch. [2], 55, 153; A. 293, 3 Anm.).

Antipyrine is a strong monacid base. It is very soluble in water and

alcohol, and crystallizes from ether in shining leaflets.

It is highly prized in medicine as an antipyretic. Its salicylate, salipyrine, acts similarly to it. This is also true of the homologue tolypyrine or γ -tolyldimethylpyrazolon, etc.

Antipyrine yields derivatives perfectly similar to those obtained from phenylmethylpyrazolon (B. 28, 623). When antipyrine is boiled with alcoholic potash it is reconverted into phenylmethylhydrazine. On heating it with sodium in toluene, conducting carbon dioxide through it at the same time, the union between the two N-atoms is broken and β -methylamidocrotonic anilide is produced (B. 25, 769):

$$\begin{array}{c} C_6H_5N-CO-CH \\ CH_2N-C \cdot CH_3 \end{array} \xrightarrow{\begin{array}{c} C_6H_5 \cdot NH-CO-CH \\ CH_2NH-C \cdot CH_3 \end{array}}$$

This is a rupture of a ring similar to that observed in the change of the pyrazolines to trimethylene diamines (p. 486).

4-Nitrosoantipyrine, (C₁₁H₁₁N₂). NO, results when antipyrine is acted upon with nitrous acid. Zinc and acetic acid reduce it to 4-amido-antipyrine, melting at 109°, the diazo-compounds of which are readily formed and yield dye-substances (A. 293, 58).

4-Oxyantipyrine, melting at 182°, results from the methylation of 4-oxy-1-phenyl-3-methylpyrazolon (p. 488) and is a compound with a pronounced phenol character (A. 293, 49).

At low temperatures methyl iodide converts antipyrine into pseudo-iodmethylate, C_0H_5 . N—— $C(OCH_3)=CH$, as it can also be prepared from $INCH_3=C(CH_3)$, as it can also be prepared from methoxymethylphenylpyrazole and methyl iodide. At higher temperatures methyl iodide and antipyrine yield 4-Methyl Antipyrine, CO. $C(CH_3)$: $C(CH_3)$: $N(CH_3)$ N. C_6H_5 , melting at 82°, and later 1-Phenyl-3,4-trimethyl Pyrazolon,

CO. C(CH₃)₃.C(CH₃): N. NC₆H₅, melting at 56° (A. 293, 1). See C. 1897, I, 540, for the action of phenols upon antipyrine. Consult A. 293, 42, for the addition of acid chlorides to antipyrine.

1-Phenyl-5-methyl Pyrazolon, CH₃. C = CH - CO - NH. NC_6H_5 , melting at 167°, is isomeric with 1-phenyl-3-methyl pyrazolon. It is produced when the corresponding pyrazolidone is oxidized with ferric chloride (B. 28, R. 78). When it is methylated isantipyrine (B. 25, R. 367; 28, 629) results. This is isomeric with antipyrine, and it is poisonous.

Pyrazolon Carboxylic Acids: Their esters are obtained from the hydrazones of β -keto- or aldehydodicarboxylic esters. The acids readily break down into CO₃ and pyrazolons.

Pyrazolon-3-carboxylic Acid, CO. CH₂ — C(COOH) — N—NH, decomposes at 250°. Its methyl ester melts at 227°. It is formed from oxalo-acetic methyl ester, chlorfumaric ester (B. 29, R. 860), or acetylene dicarboxylic ester with hydrazine (B. 25, 3442; 26, 1722). Nitrous acid converts it into an isonitroso-compound,

CO—C(NOH). C(COOH) = N—NII, melting at 201°, which yields the hydrazide of hydrazipyrazolon carboxylic acid when treated with hydrazine hydrate. The anhydride of this acid, decomposing at 126°, represents a symmetrical dicyclic nucleus:

which may also be viewed as the dilactazam of dioxosuccinic osazone (B. 26, 2057). By the elimination of carbon dioxide pyrazolon-3-carboxylic acid yields pyrazolon, obtained in various other ways (see B. 29, 249).

Pyrazolon-4-carboxylic Acid, $\dot{C}O$ —CH(COOH)—CH = N. NH. Its ethyl ester melts at 181°. It is formed, along with malonyl hydrazides, when hydrazine hydrate acts upon the ester of dicarboxyglutaconic acid, $(CO_2R)_2CH$. CH: $C(CO_2R)_3$, and when

hydrazine and the ester of ethoxymethylenemalonic acid react (B. sa, 2053). This still splits off CO₂ quite easily and becomes pyrazolon (B. sa, 988).

I-Phenylpyrasolon-4-carboxylic Acid, CO—CH(COOH)—CH = N-NCH, melts at 93° with decomposition. Its ethyl enter melts at 118°. It is produced win phenylhydrazine acts upon the enter of dicarboxyl-glutaconic acid or the enter of charmethylenemalonic enter (1, 494). The isomeric I-Phenyl-3-pyrasolon Carboxylis Acid, melting at 181°, is produced in the form of its enter from oxaloacetic enter and phenylhydrazine. Both phenylpyrasolon carboxylic acids yield the same phenylpyrasolon (n. 488: B. 28. 41).

(p. 488; B. 28, 41).

The orazones of the dioxosuccinic acid esters readily yield the ester of z-phenyl+phenylhydrazone-3-pyrazolon carboxylic acid (z). This has a red color. It makes at 154°. It is the parent substance of the valuable yellow dye tartraxine (2), the chief constituent of which is the trisodium salt of tartraxinic acid or z,p-sulphoxylphenyl-

4,p-sulphoxylphenylhydrasono-pyrasolon-3-carboxylic acid:

The latter acid can also be obtained from 1,p-sulphoxylphenyl-3-pyrasolon carbonise acid and from the diazide of sulphanilic acid, which fully demonstrates its constitutes (A. 294, 219).

PYRAZOLIDINES.

The derivatives of *tetrahydropyrazole* or *pyrazolidine* pass easily, as a general thing, into pyrazoline compounds, therefore they possess reducing properties. The simplest pyrazolidine is not yet known.

n-Phenylpyrazolidine, C_{H_2} . C_{H_2} . C_{H_2} . is an oil. It boils at 160° (20 mm.). It is formed when sodium phenylhydrazine acts upon trimethylene bromide (B. 26, R. 402). The oxygen of the air oxidizes it to phenylpyrazoline. Alkali and methyl iodide converted to the state of th

it into I-Phenyl-2-methyl Pyrazolidine, CH₂—CH₂—CH₃. N(CH₃)NC₆H₅, boiling at 175-180° (90 mm.). The reduction of the corresponding pyrazolidone products I phenyl-3-methylpyrazolidine (B. 26, 107). I,3,5-Triphenyl-2-methylpyrazolidine, melting at 110°, results in the reduction of triphenylpyrazole iodmethylate with sodium and alcohol.

Pyrazolidine carboxylic acids have been obtained by the reduction of pyrazoline carboxylic acids (B. 26, R. 282).

Keto-derivatives of the pyrazolidines:

(1) Pyrazolidones result from the interaction of hydrazines and β -haloid fatty axis or a,β -olefine carboxylic acids. If phenylhydrazine be employed, it is possible for the reaction to pursue a double course, according as the secondary or tertiary group of the hydrazine is rearranged by the carboxyl group of the acid:

INDAZOLES.

The resulting isomerides are distinguished by the fact that the I-phenyl-5-pyrazolidones have only basic properties, whereas the I phenyl-3 pyrazolidones also possess acid properties. On oxidation the pyrazolidones readily become pyrazolons, and when reduced with sodium and alcohol they are converted, in part, into pyrazolidines (see below).

Pyrazolidone, CH₂. CH₂. CO. NH. NH, boiling at 133-135°, is obtained from acrylic acid and hydrazine. It is a base. When oxidized it yields pyrazolon (J. pr. Ch.

[2], 51, 73). 1-Phenyl-5-pyrazolidone, CO. CH₂. CH₂. NH. N. C₄H₅, melting at 78°, is derived from β -haloid propionic acids by means of sodium formylphenylhydrazine, or from acrylic acid with phenylhydrazine in toluene solution (B. 28, 26). It is only basic, and when oxidized it becomes I-phenyl-5-pyrazolon, melting at 118° (p. 488).

The isomeric 1-Phenyl-3-pyrazolidone, CH₂. CH₂. CO. NH. N. C₈H₅, melting at 119-121°, and obtained from β -haloid propionic acid with free phenylhydrazine, as well as from unsym. β -phenylhydrazidopropionic ester (B. 24, R. 234), possesses acid properties also, and when oxidized becomes 1-phenyl-3-pyrazolon, melting at 154°; its n-acetyl

derivative melts at 67° (B. 29, 517).

1-Phenyl-3-methyl-5-pyrazolidone, melting at 84° and boiling at 321°, is derived from crotonic acid and phenylhydrazine or from symmetrical β -phenylhydrazidobutyric acid (B. 27, R. 687). It is a base. It readily changes to 1,3-phenylmethylpyrazolon. When methylated it yields 1,2,3-phenyldimethylpyrazolidone, hydroantipyrine, melting at 146°. It cannot be converted by oxidation into antipyrine (B. 26, 103). 1-Phenyl-

3-dimethyl-5-pyrazolidone, CO.CH₂.C(CH₂)₂NH. NC₄H₅, melting at 75°, is produced from dimethyl acrylic acid and phenylhydrazine. Boiling baryta-water decomposes it into phenylazoisovaleric acid, $C_6H_6N:N.C(CH_3)_2CH_2COOII$ (A. 292, 284). I-Phenyl-5-methyl-3-pyrazolidone, melting at 128° and obtained from unsym. β -phenylhydrazidobutyric acid, also possesses acid properties. By oxidation it yields 1,5-phenylmethyl-pyrazolon (p. 488).

(2) Diketopyrazolidines are the cyclic hydrazides of the malonic acids : 3,5-Diketopyr-

azolidine, Malonyl hydrazine, CO. CH₂. CO. NH. NH, is an oil. It is formed from malonic ester and hydrazine (B. 28, R. 159).

I-Phenyl-3,5-diketopyrazolidine, Malonyl-phenylhydrazine, melting at 192°, is obtained from the phenylhydrazide of malonic ester acid (B. 25, 1506). Consult B. 30, 1018, for its derivatives.

2. INDAZOLES.

Just as the benzopyrrols or indols correspond to the pyrrols, so do the benzopyrazoles or indazoles correspond to the pyrazoles.

There are two isomeric series of N-alkylic indazoles. The one series is produced by the action of alkyl iodides upon indazole or its homologues. The second series, called isindazoles, result synthetically from ortho-substituted a-alkylphenylhydrazines, and therefore have the alkyl residue attached to the N-atom adjacent to the benzene nucleus; consequently, in the isomeric n-alkyl indazoles the alkyl residue must be joined to the second (β -) N-atom, and the subjoined formula:

C₆H₄ CH NH, must be ascribed to the simplest indazole from which the others are derived.

Hence the real benzopryazole, C₆H₄ CH N, is the hypothetical parentsubstance of the isindazoles.

Indasoles result (1) upon heating the o-hydrazine cinnamic acids (p. 277) (E. Fischer and Tafel, A. 227, 303):

$$C_0H_4 < CH = CH \cdot COOH \longrightarrow C_0H_4 < CH > NH (+ CH_3 \cdot COOH)$$
o-Hydrazine-cinnamic Acid
Indazole.

It is singular that a lactam-like anhydride of the hydrazine-cinnamic acid is not formed in this reaction. It would contain a seven-membered ring (see p. 436). Indazole acetic acid is produced by the moderated oxidation of o-hydrazine-cinnamic acid.

(2) From the elimination of water from o-hydrazine-acetophenone or o-hydrazinephenylglyoxylic acids:

$$C_6H_4 < {}_{NH.NH_2}^{CO.COOH} \longrightarrow C_6H_4 < {}_{N}^{C} \longrightarrow NH$$

(3) n-Phenylindazoles are formed in the reduction of o-nitrobenzylanilines (B. 24, 961; 27, 2899):

:
$$C_6H_4 < {}^{CH_9-NHC_8H_5}_{NO_8} \xrightarrow{H} C_8H_4 < {}^{CH}_N > NC_8H_8.$$

(4) Further, indazoles are formed by the careful decomposition of o-diazotoluene compounds (B. 26, 2349):

(a) NO₂ .
$$C_6H_8 < \frac{CH_8}{N = NCl} \longrightarrow NO_2$$
 . $C_6H_8 < \frac{CH}{N} > NH$

p-Nitro-o-diazotoluene Chloride
(b) $C_6H_4 < \frac{CH_3}{N - N \cdot NHC_7H_7} \longrightarrow C_6H_4 < \frac{CH}{N} > NH(+NH_2 \cdot C_7H_1)$

Toluene-o-diazotoluide

Indazole.

Isindazoles are obtained (1) from o,a-alkylhydrazine-cinnamic acids or o,a-alkylhydrazine-acetophenones:

$$C_6H_4 < \frac{CH.CH.COOH}{NR.NH_2} \Rightarrow C_6H_4 < \frac{CH}{N} \times R ; C_6H_4 < \frac{CO.CH_8}{NR.NH_4} \Rightarrow C_6H_4 < \frac{C(CH_3)}{NR} \times R$$

(2) By the action of glacial acetic acid or acetic anhydride upon o-amidoaldoximes or ketoximes (B. 26, 1903; 29, 1261):

$$C_6H_4$$
 $C: NOH$ $(CH_9CO)_9O$ C_6H_4 CH $N(COCH_9)$ N .

(3) The formation of an imidazole derivative from the phenylhydrazone of o,p-dinitrophenylglyoxylic ester recalls pyrazole syntheses (B. 22, 319):

$${\rm NO_2.C_6H_3} < {\rm C(CO_2R):N.NHC_6H_5} + {\rm KOH} = {\rm NO_2.C_6H_3} < {\rm C(CO_3R) \choose N(C_6H_6)} > N + {\rm NO_2K + H_3O.}$$

a-Phenylisindazole, C₆H₄ CH N_(C₆H₅)N, melting at 142° (C. 1897, I, 763), is similarly formed from salicylaldehyde and phenylhydrazine by the action of acetic

Properties: The indazoles are usually crystalline, feeble bases, quite stable toward oxidizing agents. Chromic acid decomposes β phenylindazole into azobenzene-carboxylic acid. Hydro-compounds are obtained with difficulty. The free imide-group can be alkylized by alkyl iodicles at 100°. The isindazoles resemble the indazoles in general characteristics. The substituents of the pyrazole ring, proceeding from the nitrogen attached to the benzene nucleus, are designated with Iz- a-, β -, γ -; and those of the benzene ring, Bz- 1, 2-, 3-, 4-.

Indazole, $C_7H_6N_2$, melting at 146° and boiling at 270°, is produced, in addition to the reactions already given, by diazotizing o-amidobenzaldehyde (B. 25, 1754). Sodium nitrite converts it into nitresoindazole, $C_7H_6N_2$. NO, melting at 74°. γ -Methyl Indazole, $C_7H_6(CH_3)N_2$, melting at 113° and boiling at 281°, is obtained from o-hydrazine-acetophenone. Acetyl chloride converts it into β -acetyl- γ -methyl indazole, $C_7H_6(CH_3)$ - N_2 . COCII₃, melting at 72° (B. 24, 2380). It forms—

 β , y-Dimethyl indazole, C_1H_1 (CH₂) N_1 . CH₂, melting at 80°. β -Phenyl-indazole $C_2H_2N_2$. C_2H_3 , melting at 84° and boiling at 345°, is formed from nitrobenzyl aniline (comp. p. 492). Methyl iodide unites with it to an *iodmethylate*, melting at 188°, and s oxidized by chromic acid to azobenzene-carboxylic acid (B. 24, 3058; 27, 48). **Thenyl-indazole**, melting at 108° or 116°, is produced by the reduction of o-diazone-carboxylic acid (B. 24, 3058; 27, 48). **y-Phenyl-indazole**, melting at 108° or 116°, is produced by the reduction of o-diazone-carboxphenone. When sodium sulphite is used for this purpose there first results an anygen-containing body, $C_{18}H_{10}N_{2}O$, melting at 126°, which probably is a β -oxy-y-phenyl-indazole, that upon further reduction becomes phenyl indazole (B. 29, 1265). **The-2-Nitro-indazole**, $NO_2 \cdot C_8H_3(CN_2H_3)$, melting at 181°, is formed, together with **introcresol** (B. 26, 2349), upon diazotizing nitro-o-toluidine. B2-1,3-Nitromethyl **Indazole**, melting at 192°, is obtained from nitroxylidine (B. 29, 305). **y-Indazole** Carboxylic Acid. C.-H.-N. COOH melting with decomposition at 250°.

y-Indazole Carboxylic Acid, C, H, N, . COOH, melting with decomposition at 259°, is derived from o-hydrazine-phenyl-glyoxylic acid, which is prepared from isatinic acid (p. 258), thus completing the transition from the indol to the indazole group (B. 26, 257). When the scid is heated it breaks down into indazole and carbon dioxide.

y-Indasole Acetic Acid, C₇H₈N₂, CH₂. COOH, results from the moderated oxidation of o-hydrocinnamic acid. It melts at 169°, and decomposes into carbon dioxide and y-methyl indazole.

a,y-Dimethyl Isindazole, C_6H_4 $C(CH_3)$ N, melting at 36°, is made by the reduction of nitroso-o-ethylamido-acetophenone. Iz-a-Acetyl Isindazole, $C_7H_6N_3$. COCH₃, Iz-a-y-Acetyl Methyl- and a,y-Acetyl Phenyl Isindazole, melting at 103° and 185°, are formed by method 2 (p. 492) from o-amido-benzaldoxime, acetophenonoxime, and benzophenonoxime. Alkalies again resolve them into these oximes (B. 29, 1255). a-Ethyl-γ-isindazole Acetic Acid, C₇H₄N₂(C₂H₅)(CH₂. COOH), melting at 132°, is obtained from nitroso-o-ethylamido-cinnamic acid. See above for a-phenyl **isindazole** and nitro- a, γ -phenyl isindazole carboxylic acid.

Hydro-isindazole Derivatives: β Phenyl Dihydroindazole, $C_6H_4 < {CH_2 \over NH} > N \cdot C_6H_5$, melting at 138°, is produced by the reduction of phenyl indazole with sodium and

Bz-Nitro-a-phenyl Dihydroindazole-γ-carboxylic Acid, melting at 235°, is formed in the reduction of nitrophenyl indazole carboxylic acid (A. 264, 149).

Indazolon, or Benzo-pyrazolon, is the inner anhydride or lactazam of o-hydrazinebenzoic acid, C₆II₄< CO > NH (A. 213, 333).

Nitro-Iz, β -phenyl Indazolon is formed from the ester of nitrophenyl hydrazidobenzoic acid (B. 30, 1100). We must include here Camphylphenylpyrazolon Carboxylic Ester, C_8H_{14} $C - CO_2R$, melting at 114°, which is formed from the
ester of camphor-oxalic acid and phenylhydrazine (C. 1897, 11, 123).

The following are benzodipyrazolons:

Hexahydrobenzodipyrazolon, NH CO C₆H NH, melting at 275°, is obtained from the ester of succino-succinic acid and hydrazine.

Dicarbobenzobis-n-phenylpyrazolon, (COOH)₃C₆(-CO NH>NC₆H₅)₂, is produced by the interaction of phenylhydrazine and hydroquinone tetracarboxylic ester (Am. Ch. J. 12, 379).

3. ISOXAZOLE OR FURO[a]MONAZOLE GROUP.

Isoxazole is the azole of furfurane corresponding to pyrazole or pyrro-[a]-monazole: Furo-[a]-monazole. In accordance with similar structure the isoxazoles are produced by methods similar to those employed for the 494

preparation of the pyrazoles. The latter, as known, are obtained from the hydrazones of β -diketo-compounds, and accordingly the isoxazole result by the exit of water from the monoximes of β -diketones and β -ketone aldehydes or oxymethylene ketones (Claisen, B. 24, 3906):

Compare B. 24, R. 767, for the formation of isoxazoles from nitroparaffins by the action of alkalies.

It ferties: Those isoxazoles, in which the adjacent methine group of the N-member is substituted, are very stable bodies. When this CH-group is not substituted, a rearrangement of A-ketonic acids into nitriles occurs quite readily, especially under the influence of sodium alcoholate:

$$N = CH - CH = C_1C_6H_5)O \longrightarrow N = C - CH_5 - C(C_6H_5) = O$$
a-Phenylisoazole
Benzoyl Acetonitrile.

The isoxazoles, like the pyrazoles, are feeble bases. The substituents of the simplest hypothetical isoxazole are designated in the diagram:

$$\frac{1}{3}CH = N$$
 $\frac{1}{3}CH = CH_{\bullet}$

Methyl Isoxazole, N = C(CH₃) = CH = CH = O, boiling at 118°, is stable. It results when hydroxylamine acts upon oxymethylene acetone. There is formed at the

anne time the isomeric a-Methyl Isoxazole, $N = CH - CH = C(CH_3) - O$, boiling at 123°, which readily rearranges itself to the nitrile of acetic acid (B. 25, 1787).

 $a \cdot \beta_{ij}$. Trimethyl Isoxazole, N = $C(CH_3) + C(CH_3) = C(CH_3) + O$, melting at 3.5° and boiling at 248°, results from the action of alkalies upon methylacetylacetoxime and from nitroethane (J. Ch. Soc. 1891, 410).

See B. 24, 3912, for ring decompositions in consequence of reductions. Phenyl Methyl Isoxazole, melting at 68°, is obtained from benzoyl acetone (p. 250). When heated with alcoholic ammonia it yields 3,5-phenylmethyl pyrazole (p. 482).

Isoxazole Carboxylic Acids.—Their esters are prepared from the oximes of the ketone oxalic esters:

$$(CH_3)^{CO} = CH_2 = C(COOR) := N \cdot OH \longrightarrow (CH_3)^{C} = CH - C(COOR) = N - O$$
Acctone Oxalester Oxime
$$\beta_{1/2} = CH - C(COOR) = N - O$$

$$\beta_{1/2} = CH - C(COOR) = N - O$$

The free acids cannot be decomposed into carbon dioxide and isoxazoles. They are completely broken down when heated (B. 24, 3908).

Bi-isexazoles result from the interaction of oxalyldiketones and hydroxylamine:

$$CH_3 - CO - CH_2 - CO - CH_{2^-} - CO - CH_3 - CO -$$

Acetomyl- γ -methylisoxazolyl Ketone appears as an intermediate product. It can also be made by the condensation of γ -methylisoxazole-a-carboxylic ester with acetone (B. 24, 3910).

Isomazolons.—These are keto-derivatives of the hypothetical dihydro-isomazole or **isomazoline**. They correspond to the pyrazolons or lactazams, consequently can also be **designated** as *lactazones* or *lactoximes*. They result when the oximes of the β -ketonic exters lose alcohol (B. 24, 140; 30, 1159; A. 296, 33):

$$HO.\ N = C(CH_{\mathfrak{g}}).\ CH_{\mathfrak{g}} - COOR \longrightarrow O.\ N = C(CH_{\mathfrak{g}}) - CH_{\mathfrak{g}} - CO.$$

A series of compounds, obtained from glyoxal, methylglyoxal, phenylglyoxal, etc. (also their oximes), by the action of hydroxylamine hydrochloride, can also be considered as the oximes of isoxazolon derivatives (comp. B. 30, 1287).

The isoxazolons, similarly to the pyrazolons, can be variously formulated:

I.
$$\stackrel{\text{CH}_2-\text{CO}}{\stackrel{\text{L}}{\text{CH}}=\text{N}} > 0$$
 II. $\stackrel{\text{CH}-\text{CO}}{\stackrel{\text{L}}{\text{CH}}=\text{NH}} > 0$ III. $\stackrel{\text{CH}=\text{C(OH)}}{\stackrel{\text{L}}{\text{CH}}===\text{N}} > 0$.

The isoxazolons have a very pronounced acid nature. They decompose the alkaline earth carbonates in the cold, and form salts not only with metals, but also with ammonia and primary amines. The constitution of these salts varies. Ethers result from the action of alkyl iodides upon the silver salts. Methylamine is liberated when phenyl-isoxazolon-methyl ether is distilled with caustic potash. The methyl group is therefore probably linked to nitrogen, and the compound is derived from formula II (A. 295, 37).

37). γ -Methyl Isoxazolon, $C_4H_5NO_2$, melting at 170°, is made from the oxime of acetoacetic ester. Barium salt, $(C_8H_7O_3N_2)_3Ba+1\frac{1}{2}H_2O$. The ammonium salt, $(C_8H_7O_3N_2)_3Ba+1\frac{1}{2}H_2O$. When the oxime of acetoacetic ester is condensed in the presence of diazobenzene salts the phenylhydrazone of y-methyl-p-ktoisoxazoline, $(C_4H_3NO_2):NNHC_6H_5$, melting at 192°, results. The condensation of the same oxime in the presence of ketones or aldehydes gives rise to Isopropylidene and Benzylidene Methyl Isoxazolons, $(C_4H_3NO_2):C(CH_3)_2$, melting at 121°, and $(C_4H_3NO_2):C(CH_3)_2$, melting at 121°, and $(C_4H_3NO_2):C(CH_3)_3$,

Isomorphylatene and Belleysteine methyl isomorphylatene, $(c_4 n_3 n_{12})$; $(c_1 n_3)_2$, melting at 121°, and $(C_4 H_3 nO_2)$; $(C_4$

 $O-N=C(C_6H_5)-CH-C$: (NII), melting at 111°, results from cyanacetophenone, C_6H_5 . CO. CH_2 . CN, or benzodiacetonitrile and hydroxylamine (B.27, 1095; Jr. pr. Ch. [2], 47, 124). γ -Phenyl-a-benzoyl- β -isoxazolon, melting at 175°, is obtained from benzoyl formoin (p. 381) and hydroxylamine (B. 25, 3468; compare B. 30, 1290):

$$\begin{array}{c} \textbf{C_6H_5CO-CO-CH(OH)-CO.C_6H_5} + \textbf{NH_2OH---O-N=C(C_6H_5)-CO-CH.CO.C_6H_5} \\ \textbf{Benzoyl Formolin} \end{array}$$

Compare B. 30, 1085, for the so-called pyroxolon carboxylic ester, C₃H₂NO₂. CO₂R, a reaction product of hydroxylamine and the ester of dicarboxyglutaconic acid.

4. INDOXAZENE OR BENZISOXAZOLE GROUP.

The benzisoxazoles or indoxazenes are obtained from the oximes of o-haloid or o-nitrobenzophenones (p. 347; B. 25, 1498) (compare method of formation 3 under the isindazoles, p. 492):

498

μ-Methyl Glyoxaline, Glyoxal Ethylin, Paraglyoxal Methylin, C₂H₂(CH₂)N₂, melting at 137° and boiling at 267°, results from the rearrangement of n-methyl glyoxaline (see above), or from glyoxal, acetaldehyde, and ammonia. Ethyl iodide converts it into μ -Methyl-n-ethyl Glyoxaline, $C_1H_2(CH_2)N_2 \cdot C_2H_3$, boiling at 213°, which is also formed from diethyl oximide chloride, and manifests physiological actions similar to those of atropine. μ -Ethyl Glyoxaline, Glyoxal Propylin, C₃H₂(C₂H₃)N₂, melts at 80° and boils at 268°.

a-Methyl Glyoxaline, C3H3(CH3)N2, boils at 263°. It is prepared from its mer-

captan by method 2 (p. 496) (B. 26, 2204).

a,β,u-Trimethyl Glyoxaline, C₁(CH₃)₃N₂H, melting at 183° and boiling at 271°, is made from diacetyl, ammonia, and aldehyde.

 β_{μ} -Diphenyl Glyoxaline, $C_3H(C_8H_5)_3N_2H$, melting at 162°, is produced on heating β_{μ} -diphenyl oxazole (p. 503) to 300° with alcoholic ammonia; also by the condensation of phenyl-a-amidoacetonitrile and benzaldehyde by means of hydrochloric acid (compare method of forming oxazoles, p. 502) (B. 29, 2103):

$$\begin{array}{c} C_{e}H_{5}CH-NH_{2}\\ \downarrow\\ CN \end{array} + HOC-C_{e}H_{5} \xrightarrow{\qquad } \begin{array}{c} C_{e}H_{5}C-NH\\ \downarrow\\ CH-N \end{array} \subset C_{e}H_{5}.$$

 a,β,μ . Triphenyl Glyoxaline, Lophine, melting at 275°, is produced:

(1) From benzil, benzaldehyde, and ammonia.

(2) When hydrobenzamide is distilled or amarine oxidized.
(3) By the reduction of triphenyl cyanidine or triphenyl tricyanogen; ammonia is eliminated.

(4) From benzamidine and benzoln (B. 29, R. 673). Lophine (from λόσος, tuft of feathers, alluding to its tufted crystalline form) exhibits in marked degree the property of phosphorescing when shaken with alcoholic potash; it is then decomposed into ammonia and benzoic acid. Like the glyoxalines, it does not form an acetate.

The halogen derivatives of the glyoxalines result from substitution; also by the splitting off of hydrogen chloride from the dialkyloximide chlorides. Tribrom-glyoxaline, C₃Br₃N₂II, melting at 214°, is formed from glyoxaline and bromine. Chlor-n-methyl Glyoxaline, C₃II₂ClN₂, CH₃, boiling at 205°, and Chlor-n,µ-dimethyl Glyoxaline, C₃IICI(CH₃)N₂, CH₃, boiling at 218°, are obtained from dimethyl- and diethyloximide chloride.

Sulphydro-derivatives are formed by condensation from acetalyl or acetonyl thiureas

and similar bodies (p. 496):

μ-Imidazolyl Mercaptan, C₃H₃(SH)N₂, melting at 222° with decomposition, is changed by methyl iodide to imidazolyl-\(\mu\)-methyl sulphide, C₃H₃(SCH₃)N₂, melting at 139° (B. 25, 2359). $a_1\beta$ -Diphenyl Glyoxaline- μ -mercaptan, $C_3(C_6H_5)_2HN_2(SH)$,

hydroglyoxalines, or glyoxalidines, result (1) from the acidyl-compounds of ethylene diamine:

$$\begin{array}{c} \text{CII}_2\text{--NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_5 \\ \downarrow \\ \text{CII}_4\text{--NII}\text{--CO}\text{--C}_6\text{H}_5 \end{array} \longrightarrow \begin{array}{c} \text{CH}_2\text{--N} \\ \downarrow \\ \text{CH}_4\text{--NH} \end{array} \longrightarrow \begin{array}{c} \text{CH}_2\text{--N} \\ \text{CH}_4\text{--NH} \end{array} \longrightarrow \begin{array}{c} \text{C} \cdot \text{C}_6\text{H}_6 (\text{+ C}_6\text{H}_6\text{COOH}). \end{array}$$

(2) They are very probably the compounds formed from allyl acetamide and allyl benzamide by means of the hydrochlorides of aromatic bases (B. 28, 1665):

p-Methyl Glyoxalidine, Lysidine, C₄H₈N₂ = CH₂-N C . CH₃, melting at 105° and boiling at 195-198°, is formed on heating ethylenediamine hydrochloride with sodium acetate. It forms a very easily soluble uric acid salt, and therefore has been recommended as a relief from gout (B. 27, 2952). The homologous glyoxalidines—e. g., μ-ethyl-, μ-propyl glyoxalidine, etc., (B. 28, 1173, 1176)—behave similarly. Benzoyl chloride and alkali resolve methyl glyoxalidine into acetdibenzoyl ethylene

diamine (B. 28, 3068). μ-Phenyl Glyoxalidine, Ethylenebensamidine, C₂H₅(C₂H₅)N₂, melting at 101°, is

also obtained from ethylenediamine and thiobenzamide (B. 25, 2135).

asso obtained from ethylenediamine and thobenzamide (B. 25, 2135).

$$a_1\beta_1\mu$$
-Triphenyl Dihydroglyoxaline, Amarine,

 $C_{\mathbf{H}_5}$. $C - NH$
 $C_{\mathbf{H}_6}$. $C - NH$

ment of hydrobenzamide. Alkyl iodides convert it into dialkyl derivatives, hence it must contain two imide groups. It yields lophine upon oxidation (p. 498). Furfurin,

or trifuryldihydroglyoxaline, is analogously constituted (p. 450).

Biaglyoxalidine, (C₃H₅N₂)₃, melting at 290-300°, is a condensation product of rubeanic acid and ethylenediamine (B. 24, 1846):

Tetrahydroglyoxalidines have been obtained from ethylene aniline and aldehydes (B. 20, 732):

$$\begin{array}{c} \text{CH$_2$--NH$. C_6H$_6$} \\ \text{CH$_2$--NII$. C_6H$_6$} + \text{CHO} . & \text{C$_6$H$_6$} = \begin{array}{c} \text{CH$_2$--N(C$_6$H$_6$)} \\ \text{CH$_2$--N(C$_6$H$_6$)} \end{array} \\ \text{Triphenyltetrahydroglyoxaline, m. p. 137°.} \end{array}$$

We must include with the keto-, thio-, and imido-substitution products of hydroglyoxalines a series of cyclic urea-, thiourea-, and guanidine-derivatives, which for the

most part have been already described with the fatty compounds. I. Ketoglyoxalidines, imidazolons, or ureines, result from the inner condensation CH—NH

a-ureido-keto-compounds: Imidazolon, | CH—NH CO, melting at 105°, is obof a-ureido-keto-compounds: Imidazolon,

tained from acetyl urea (p. 496). Different ureines have been obtained from benzoin and benzil by means of various ureas (compare B. 25, 2357; 27, 1083, 1144, 2203; Gaz. chim. Ital. 19, 573).

2. Keto- and Thiotetrahydroglyoxalines are the cyclic alkylen ureas and thiourease.g., ethylene urea and -thiourea (1, 400, 409).

3. Diketo- and imidoketotetrahydroglyoxalines are found in the hydantoins and glycocyanidines-e.g., hydantoin, creatinine, etc. (1, 401, 413).

4. Triketo- and imidodiketotetrahydroglyoxalines: oxalyl urea or parabanic acid (1, 505) and oxalyl guanidine (B. 26, 2552).

6. BENZOGLYOXALINES, OR BENZIMIDAZOLES.

The benzimidazoles, sometimes called cyclic amidines, anhydro-bases, and aldehydines, contain the glyoxaline or imidazole ring in union with a benzene ring:

$$CH = CH - C - NH$$

$$CH = CH - C - NH$$

$$CH = CH - C - NH$$

Their intimate connection with glyoxaline becomes very evident from the fact that benzimidazole becomes glyoxaline dicarboxylic acid when it is oxidized (p. 496).

Formation of the Benzimidazoles:

(1) By the condensation of o-phenylenediamines with carboxylic acids, or their anhydrides or chlorides. An exit of water occurs (Ladenburg, B. 8, 677; 11, 826). Acidyl compounds are produced at the same time as intermediate products:

$$\begin{array}{c} C_0H_4 < \stackrel{NH_2}{NH_3} + CH_3 \cdot COOH \longrightarrow C_0H_4 < \stackrel{NH_3}{NH_3} \cdot CO \cdot CH_3 \longrightarrow C_0H_4 < \stackrel{NH_3}{N} C \cdot CH_3 \\ \text{o-Phenylenediamine} \\ \end{array} \\ \begin{array}{c} C_0H_4 < \stackrel{NH_3}{N} C \cdot CH_3 \longrightarrow C_0H_4 \longrightarrow C_0H$$

The diacidyl-o-phenylenediamines also yield benzimidazoles (B. 23, 1876; 25, 1992). The anhydrides of dibasic acids react like those of the monobasic—e. g., succinic anhydride and o-phenylenediamine form benzimidazole- μ -propionic acid (B. 27, 2773). The o-naphthylenediamines behave like the o-phenylenediamines.

(2) Benzimidazoles are also produced by the reduction of acidylated o-nitranilines, when acidylated o-phenylenediamines are also formed as intermediate products (Ho-

brecker, B. 5, 920):

$$C_{\mathbf{6}}H_{\mathbf{4}} < \stackrel{\text{NH.CO.CH}_{\mathbf{9}}}{\longrightarrow} \left[C_{\mathbf{6}}H_{\mathbf{4}} < \stackrel{\text{NH.CO.CH}_{\mathbf{9}}}{\longrightarrow} \right] \longrightarrow C_{\mathbf{6}}H_{\mathbf{4}} < \stackrel{\text{NH}}{\nearrow} C.CH_{\mathbf{9}}$$

(3) N-alkylic benzimidazoles result when aldehydes act upon o-diamines (aldehydines of Ladenburg, B. 11, 590). The dialkylidene-o-diamine, which probably first appears, rearranges itself at once into the n-alkylic imidazole (B. 20, 1585). The non-alkylized imidazole is produced as a by-product from the monoalkylidene body:

$$\begin{array}{c} C_{6}H_{4} > \stackrel{N}{\underset{C}{N}} = \stackrel{CH}{\underset{CH}} \cdot \stackrel{CH}{\underset{CH_{3}}{\longleftarrow}} \\ C_{6}H_{4} < \stackrel{N}{\underset{N}{\longleftarrow}} = \stackrel{CH}{\underset{CH}{\longleftarrow}} \cdot \stackrel{CH}{\underset{CH_{3}}{\longleftarrow}} \\ C_{6}H_{4} < \stackrel{N}{\underset{NH_{2}}{\longleftarrow}} \\ \end{array} \begin{array}{c} C \cdot CH_{3} \\ C_{6}H_{4} < \stackrel{N}{\underset{NH_{2}}{\longleftarrow}} \\ \end{array} \begin{array}{c} C \cdot CH_{3} \\ C \cdot CH_{3} \\ \end{array}$$

Mono-alkylic o-diamines yield benzimidazoles (B. 25, 2826).

Properties: The benzimidazoles behave very much like the glyoxalines (p. 496); however, the basic properties are slightly less than the salt-forming power of the imidogroup. Most of the benzimidazoles are soluble in aqueous alkalies. Alkyl residues are easily introduced into the imide group; acid residues, with more difficulty. Benzoyl chloride and sodium hydroxide decompose even at 0°, just as in the case of the glyoxa-lines, the imidazole ring with the production of dibenzoylated o-diamines. They are very stable toward reducing and oxidizing agents. Certain derivatives of benzimidazole can dye cotton without the help of mordants (B. 26, 2760). In this respect they resem-

ble the benzoxazoles (p. 503) and benzothiazoles (p. 507).

The number of known benzimidazoles is very great. See Kühling: Stickstoffhaltige

Ortho-condensationsproducte, S. 177-210.

Benzimidazole, o-Phenylene Formamidine, CaH, NH CH, melting at 167°, is obtained from formic acid and o-phenylenediamine, as well as by the action of chloroform and potash upon o-phenylenediamine (B. 28, R. 392). Potassium permanganate oxidizes it in part to glyoxaline dicarboxylic acid.

µ-Methyl-benzimidazole, o-phenylene acetamidine, CoH, NH C. CH, melts at 176°.

 μ -Phenylbenzimidazole, phenylene benzamidine, C_6H_4 N C . C_6H_5 , melting at 291°, also results from the rearrangement of o-amidobenzophenonoxime (B. 24, 2386; **29**, R. 358).

$$\mu$$
-Methyl Tolimidazole, o-Toluylene Acetamidine, CH_3 . C_6H_3 . NH

melting at 199°, and obtained from m,p-toluylenediamine with glacial acetic acid or acetaldehyde, unites with methyl iodide to n,μ -dimethyl tolimidazole, melting at 142°, then to its *iodmethylate*, melting at 221°. Silver nitrate precipitates the *silver salt*, $C_1H_2(C_2H_2N_2Ag)$. Chloride of lime replaces the imide hydrogen by chlorine, which readily exchanges its place with a benzene hydrogen atom:

$$C_1H_0 < \frac{N}{NCl} > C.CH_0 \longrightarrow C_1H_0Cl < \frac{N}{NH} > C.CH_0.$$

This chlorination may be continued until all of the hydrogen atoms of the benzene nucleus have been replaced by chlorine and there is finally obtained

n-Acetyl- μ -methyl Tolimidazole, $C_1H_0(C_2H_3N_3, COCH_3)$, is formed when acetyl chloride acts upon the silver salt. The n-bensoyl derivative, melting at 92°, is formed from the base and benzoyl chloride, while benzoyl chloride and sodium hydroxide produce dibenzoyltoluylenediamine. μ -Methyltolimidazole condenses with benzaldehyde

dride to a phthalone (compare quinophthalone), which is oxidized by potassium permanganate to tolimidasole-μ-carboxylic acid, C₈H₇N₂. COOH. Compare B. 25, 2712, upon polymeric benzimidazoles.

Bisbenzimidazoles are made by reducing the o-nitro-oxanilides (A. 209, 257):

$$C_{e}H_{4} \stackrel{NH-CO-CO-NH}{\nearrow} C_{e}H_{4} \stackrel{H}{\longrightarrow} C_{e}H_{4} \stackrel{N}{\nearrow} C_{e}C \stackrel{N}{\nearrow} N_{H} C_{e}H_{4}.$$

Bisbenzimidazole, m. p. above 300°.

Benzobisimidazoles are formed from the o-diamidobenzimidazoles and carboxylic acids (B. 22, 1652):

$$CH_{3}. C \bigvee_{NH}^{N} C_{6}H_{2} \bigvee_{NH_{2}}^{NH_{2}} + CH_{3}.COOH \longrightarrow CH_{3}. C \bigvee_{NH}^{N} C_{6}H_{2} \bigvee_{NH}^{N} C.CH_{3}$$
o-Diamidobenzo- μ -methylimidazole

Benzobis- μ -methylimidazole, m. p. 145°.

Bensimidazole hydrides, bensimidazolines, are not known with certainty. The primary products resulting from the interaction of monoalkylic o-diamines and aldehydes are considered as such. They give up hydrogen and readily change to benzimidazoles (B. 25, 2827). The condensation products of acetoacetic ester with o-tolylenediamine (B. 25, 606) behave similarly. Methylene iodide and dibenzene-sulphon-o-phenylenediamine yield dibenzenesulphonmethylene-o-phenylenediamine,

 $C_6H_4 < N(SO_2C_6H_5) > CH_2$, melting at 148°. It can be considered as a derivative of the simplest benzimidazoline. In an attempt to split off the benzene sulphon-groups with hydrochloric acid it was resinified (B. 28, R. 756).

These substances can be considered as derivatives of hydrobenzimidazoles, which result in the moderated reduction of acidylated o-nitranilines with ammonium sulphide (B. 22, 1396):

Acet-o-nitrotoluide Oxy-µ-methyl Tolimidazole

These are relatively stable bodies, which yield benzimidazoles when they are distilled with sinc-dust.

502

The cyclic phenylene ureas, -thioureas, and -guanidines are keto-, thio-, and imido-bensimidasolines, which result from o-diamines with COCl, and CSCl, or CS₂, with urea and thiourea or ammonium sulphocyanide, with phenyl mustard oil and carbodi-imide (p. 95):

$$\begin{array}{l} C_{g}H_{4} < \stackrel{NH_{2}}{NH_{3}} + \text{COCl}_{2} \text{ (or CSCl}_{2}) \longrightarrow C_{g}H_{4} < \stackrel{NH}{NH} > \text{CO (or } C_{g}H_{4} < \stackrel{NH}{NH} > \text{CS)} \\ C_{g}H_{4} < \stackrel{NH_{2}}{NH_{3}} + \text{C(NC}_{g}H_{5})_{2} \longrightarrow C_{g}H_{4} < \stackrel{NH}{NH} > \text{C: NC}_{g}H_{5} \\ Carbodiphenylimide & Phenylenephenyl Guanidine.} \end{array}$$

In many respects these bodies behave like oxy-, sulpho-, hydro-, and amido-derivatives of benzimidazoles, and permit a choice from the two formulas:

I.
$$C_6H_4 < \frac{NH}{NH} > CO(S. NH)$$
 II. $C_6H_4 < \frac{N}{NH} > C. OH(SH, NH_4)$.

o-Phenylene Urea, Bensimidazolon, $C_0H_4(N_2H_3CO)$, melting at 308°, is also obtained from o-amidophenylurethane (B. 12, 1296; 23, 1047). o-Toluylene Urea, $C_1H_6(N_2H_3)CO$, melting at 290°, also results in the saponification of μ -ethoxytolimidazole, $C_1H_6(N_2H):C(OC_2H_6)$, melting at 163°. The latter is the reaction product of imidocarbonic ester and o-toluylenediamine.

o-Phenylenesulpho-urea, *Thiobensimidazoline*, C₈H₄(N₂H₂)CS, melting at 298° with decomposition, is obtained from phenylenediamine sulphocyanide (A. 221, 9;

228, 244).

 O-Phenylene-phenyl Guanidine, μ-Anilidobensimidasoline, C_eH₄(CN₃H₂C_eH₅), melting at 188°, is obtained from carbodiphenylimide and o-phenylenediamine.

The oxazoles and thiazoles correspond to the imidazoles. The latter were regarded as cyclic amidines (p. 495), and the former may be looked upon as cyclic imido-ethers and alkylene thioamides (1, 269). As a rule, these bodies are as little changed by reduction to hydride bases as the glyoxalines or imidazoles; they remain unaltered or are decomposed (comp. B. 29, 2381).

7. OXAZOLES OR FURO-[b]-MONAZOLES.

The oxazoles or furo-[b]-monasoles, N=CH O, are isomeric with the isoxazoles

(furo-[a]-monazolon, p. 493). Oxazoles are produced (1) by the condensation of a-haloid ketones with acid-amides (B. 20, 2576; 21, 2195):

It may be assumed that here the ketone and amide react in the hydroxyl form.
(2) When concentrated sulphuric acid acts upon benzoin and acid nitriles (B. 26, R. 496):

$$\begin{array}{c} C_{8}H_{5}.CO \\ C_{8}H_{5}.CH.OH \end{array} + N \equiv C.CH_{8} \longrightarrow \begin{array}{c} C_{8}H_{8}C - N \\ C_{6}H_{5}CH-O \end{array} C.CH_{8}$$
Benzoln
$$\begin{array}{c} C_{6}H_{5}CH - O \\ O_{6}B-Diphenyl-\mu-methylozasoke. \end{array}$$

(3) When hydrochloric acid gas acts upon mandelo-nitrile (and homologues) and benzaldehydes (B. 29, 2097):

$$\overset{C_{\mathfrak{g}}H_{\mathfrak{g}}.\ CHOH}{C \equiv N} + OCH.\ C_{\mathfrak{g}}H_{\mathfrak{g}} \xrightarrow{\hspace*{1cm}} \overset{C_{\mathfrak{g}}H_{\mathfrak{g}}.\ C}{C = O} C.\ C_{\mathfrak{g}}H_{\mathfrak{g}}.$$

The oxazoles are feeble bases. They break down into acids and amines on evaporation with hydrochloric acid. Oxidants and reducing agents frequently rupture the oxazole ring with great ease. The parent substance of the group is not known. β -Phenyl Oxazole, $C_2H_2(C_2H_5)$ NO, melting at 46° and boiling at 222°, is made from formamide and bromacetophenone. β -Phenyl- and a,β -Diphenyl- μ -methyl Oxazole, melting at 45° and boiling at 242°, and melting at 44° and boiling at 192-195° (15 mm.); see above. a-Methyl- μ -phenyl Oxazole, from benzamide and chloracetone is converted by alcoholic ammonia into above the decay and the acetone, is converted by alcoholic ammonia into phenylmethyl glyoxaline.

a,u-Diphenyl Oxazole, melting at 74° and boiling above 360°, is formed from benzamide and phenylbromacetaldehyde by method 1, and, together with benzalmandelic amide, from the nitrile of mandelic acid and benzaldehyde by method 3 (B. 29, 205). Chromic acid oxidizes it to phenylglyoxylbenzamide, C₆H₆CO.CO.NH.CO.C₆H₆, while sodium and alcohol reduce it to benzylphenyloxethylamine, C₆H₅CH₂.NH.CH₂.-CH(OH)C₆H₆. Nitric acid apparently produces a nitrodiphenyl oxazole. It is converted into diphenylimidazole when heated with ammonia.

Dihydro-oxazoles, oxazolines, are produced by the condensation of β -haloid alkylamides with alkali (B. 22, 2220):

μ-Phenyloxazoline, boiling at 243°, is broken down, in the reduction with sodium

and amyl alcohol, to oxethylbenzylamine, OHCH₂. CH₂. NHCH₂C₆H₅ (B. 29, 2382).

μ-Methyl Oxazoline is an oil. Its picrate melts at 159° (B. 23, 2502).

β-Methyl-μ-phenyl Oxazoline, boiling at 244°, is obtained from β-brompropylbenzamide, also from allylbenzamide, C₆H₅. CO. NII. CH₂. CH: CH₂, with concen-

trated sulphuric acid (B. 26, 2840) (compare glyoxalidines, p. 499).

Amido-oxazolines or imidotetrahydro-oxazoles are the so-called allylene-ψ-ureas.

compounds result from the action of potassium cyanate upon β -bromethyl- and -propylamine. a,β -Diphenyl- μ -amidoxazoline, melting at 154°, is formed from diphenyloxethylamine (p. 372) and potassium cyanate (B. 28, 1899).

Derivatives of a ketotetrahydro-oxazole have been obtained from carbamic- β -haloid

alkyl esters by the elimination of hydrochloric acid (B. 25, R. 9):

8. BENZOXAZOLES.

These, like the production of benzimidazoles from o-phenylene diamines, result upon heating o-amidophenols with carboxylic acids (p. 153):

$$\begin{array}{ll} C_0H_4 < \stackrel{OH}{NH_3} + CH_3 \,.\; CO_2H = C_0H_4 \stackrel{O}{\diagdown} CCH_3 + 2H_4O. \\ \text{o-Amidophenol} \end{array}$$

504

The benzoxazoles, also called alkenylamidophenols, are weak bases They are resolved into their components on digesting them with acids Some benzoxazole derivatives are substantive cotton dyes (B. 26 1127).

Benzoxazole, Methenylamidophenol, CeHe N CH, melts at 31° and boils at 183° μ-Methyl Benzoxazole, ethenyl amidophenol, boils at 201°. μ-Phenyl Benzoxazole melting at 103°, is also formed in the reduction of benzoyl-o-nitrophenol (B. 9, 1526; 29, R. 358; A. 210, 384).

μ-Amidophenyl Toluoxazole, CH₂. C₆H₃ N C. C₆H₄NH₂, melting at 188°, is produced in the reduction of p-nitrobenzoyl-m-nitro-p-cresol. By combination of its diazo-derivative with β -naphthol, etc., carmine-red, acid-stable substantive cotton dyes

Oxy- and this-derivatives of the benzoxazoles are obtained from o-amidophenols with COCI, or CICO, R and CS, or CSCI, Amido-derivatives result on heating thio- or oxycompounds with amines. Here, as in the case of analogous benzimidazole compounds, two formulas may be considered for these bodies:

Isomeric alkyl compounds are derived from the two forms of μ-oxybenzoxazole, which may be distinguished as lactime and lactam ethers or O- and N-alkyl derivatives. The amidobenzoxazoles exhibit similar conditions.

u Oxybenzoxazole, Carbonyl Amidophenol, C₁H₅NO₂, melting at 137°, is insoluble in alkalies. Methyl iodide converts it into an n-ethyl derivative.

n Ethyl Benzoxazolon, $C_6H_6 < \frac{O}{N(C_4H_8)} > CO$, melts at 29°. μ -Ethoxybenzoxa-

zole, C₆H₄ COC₂H₅, is formed from imidocarbonic ester and o-amidophenol (B. 19,

2655). μ Thiobenzoxazole, C_7H_8NSO , melting at 193-196°, is soluble in alkalies and ammonia. It is obtained from amidophenol hydrochloride by the action of potas-

sium xanthogenate; also from o oxyazobenzene and CS2.

 μ -Anilidobenzoxazole, $C_1H_3N_2O(C_6H_6)$, melting at 137°, is produced simultaneously. The latter is also formed on heating thiobenzoxazole with aniline. μ -Amidobenzoxazole, C₁H₅N₂O, melting at 130°, is isomeric with o-phenylene urea (p. 502). It results on splitting off hydrogen sulphide from o-oxyphenylsulphourea by means of mercuric oxide. μ Phenylimido n-ethylbenzoxazolon, $C_6H_4 < \frac{O}{N(C_2H_5)} > C: N \cdot C_6H_9$ is formed from n-ethyl benzoxazolon and aniline (J. pr. Ch. [2], 42, 450).

9. THIAZOLES OR THIO-[b]-MONAZOLES.

Just as the oxazoles are prepared from acid-amides, so the thiazoles or thio-[b]-mon-

N CII azoles, CII = CII > S, are obtained from the thio-amides and a-haloid ketone derivatives:

Further, this acid and its homologues result from the action of nitrous acid and alcohol upon \(\mu\)-amidothiazoles just as the benzene hydrocarbons are obtained from the milines.

Behavior: Thiszole may be derived from pyridine, just as thiophene is derived from benzene—i. e., by imagining a CH: CH-group replaced by sulphur. Accordingly, the thiasoles show a like agreement or similarity in their physical and in part in their chemical properties with the pyridines, just as the thiophenes do with the benzenes.

The thiazoles are tertiary bases, forming addition products with alkyl iodides. As a

rule, they are stable toward oxidizing agents; chloric acid, however, destroys them.

Thiazole, C₃H₃NS, boiling at 117°, has an odor like that of pyridine. It results when N₂O₃ and alcohol act upon \(\mu\$-amido-thiazole, C₃H₃NS, HCl. AuCl, melts with decomposition at 248-250°. C₃H₃NS, HgCl, melts at 202-204°. a-Methyl Thiazole, C₃H₄(CH₃)NS, boiling at 232°, is obtained from its amido-compound and by distilling methyl oxythiazole with zinc-dust (A. 250, 279). The isomeric \(\mu\$-methyl thiazole, boiling at 128°, with an odor like picoline (see this), is prepared from monochloracetone and this cetamide. $a_{,\mu}$. Dimethyl This zole, boiling at 143°, from chloracetone and this cetamide, when reduced by sodium and alcohol is resolved into ethyl propylamine

and hydrogen sulphide. It condenses, like the a-methylated pyridines, with formic aldehyde to an alkine, C₃HNS(CH₃)(CH₂·CH₂OH) (B. 27, 1009).

Trimethyl Thiazole, C₃(CH₃)₃NS, melts at 167°. a-Phenyl Thiazole melts at 52° and boils at 273°. Triphenyl Thiazole, melting at 87°, is formed from thiobenzamide and bromdesoxybenzoln or desylbromide.

Haloid thiazoles are prepared by acting with concentrated haloid acids upon diazothiazoles:

 μ -Chlorthiazole boils at 145° and μ -bromthiazole boils at 171°. μ-Amidothiazoles result from the action of a-haloid keto-compounds upon thioureas:

$$\begin{array}{c} CH_3 \cdot CO \\ H_2CCI \\ \text{--Chloracetone} \end{array} + \begin{array}{c} NH \\ HS \\ Thiourea \end{array} \longrightarrow \begin{array}{c} CH_2 \cdot C - N \\ HC - S \\ \rho - Methyl - \mu - amidothiazole. \end{array}$$

Substances are formed from the symmetrical dialkylic thioureas which are derived from imidothiazoline. Consult A. 265, 110, for isomeric monalkylamidothiazoles.

The amidothiazoles are similar to the anilines. They can be converted into diazocompounds, and through these into haloid thiazoles, thiazoles, thiazole-azo-dyes, etc.

μ-Amido-thiazole, C₃H₂(NH₂)NS, melting at 90°, may be prepared from dichlorether and thiourea. Its nitrate is converted by N₂O₃ into Diazothiazole Hydrate, C₃H₂(. N:NOH)NS, which yields yellow to brown-colored azo-dyes with resorcinel, naphthol, etc. (A. 246, 40). Methyl-μ-amido-thiazole, C₃H(CII₃)(NH₂)NS, melting at 42° and boiling at 136° (30-40 mm.), is formed from chloracetone and thiourea or ammonium sulphocyanide (B. 20, 3127). Phenyl-μ-amidothiazole, C₃H(C₆H₅). (NH) NS from a chloracetophenome (P. 241) yields the number of the color of t (NH2)NS, from w-chloracetophenone (p. 231), yields phenyldiazothiazole hydrate (A. 261,

 β ,n-Dimethyl- μ -methyl Imidothiazoline, HC = S $C: NCH_3$, melting at 96°, $CH_3C = N \cdot CH_3$

is obtained from chloracetone and symmetrical dimethyl thiourea. Oxythiazoles are obtained from a-sulphocyan ketones by the action of alkali:

$$\begin{array}{c} C_gH_\delta \cdot CO \\ H_1C \cdot SCN \\ \hline \\ Salphocyan-acetophenone \\ \end{array} \xrightarrow{\begin{array}{c} C_gH_\delta \cdot CO \\ H_2C \\ \hline \\ Carbamthioacetophenone \\ \end{array}} \begin{array}{c} CO \\ H_2C \\ \hline \\ CO \\ \hline \\ CO \\ \end{array} \xrightarrow{\begin{array}{c} C_gH_\delta C \\ HC \\ \hline \\ CO \\ \end{array}} \begin{array}{c} C(OH) \\ CO \\ \hline \\ CO \\ \end{array}$$

 β -Methyl- μ -oxythiazole, $C_1H(CH_3)(OH)NS$, melting at 160°, results from the exit of carbon dioxide from its carboxylic acid and also when alkalies act upon sulphocyanacetone (A. 259, 297; B. 25, 3652). a-Phenyl- μ -oxythiazole melts at 204° (A. 249, 16) (see above).

Mercaptethiaseles result upon heating a-chlorketones with ammonium dithiocarbami-

nate:

CH - S CH₃ . C - N C. SH, melts at 90°. β -Methyl- μ -mercapto-thiazole,

 β -Phenylmercapto-thiazole melts at 168° (B. 26, 604).

Thiazole Carboxylic Acids: Their esters are produced in the condensation of chloracetoacetic ester, chloroxalo-acetic ester, etc., with thioamides:

Furthermore, the amido-, oxy-, and mercapto-thiasole carboxylic acids are formed by reactions similar to those employed for the amido-, oxy-, and mercapto-thiazoles, if instead of the ketone derivatives the corresponding ketone carboxylic acids are introduced into the reactions.

β-Methylthiazole-a-carboxylic Acid, C₃(CH₃)HNS(COOH), melts at 257°. It ester is obtained from amidomethylthiazole carboxylic ester (see below) by converting it into chlorthiazolecarboxylic ester and then reducing the latter.

 μ -Methyl- a,β -thiazole Dicarboxylic Acid, C_3 (CH₃)(COOH)₂NS, melts with decomposition at 169°. It is formed from chloroxaloacetic ester and thiacetamide. μ-Methyl-β-thiazylacetic Ester, C₃H(CII₃)(CH₂. CO₂R)NS, boiling at 239°, is formed from γ-bromacetoacetic ester and thiacetamide.

μ-Amidothiazole-β-carboxylic Acid, Sulphuvinic Acid, C₂HSN(NH₂)COOH-(+ 2II₂O), decomposes at 245°, and is formed from dibrompyroracemic acid. Its ester, melting at 173°, is produced from monobrompyroracemic ester and thioures (A. 261, 25).

 μ -Amido-methylthiazole- β -carboxylic Ester, melting at 175°, is obtained from a-chloracetoacetic ester and thiourea. Its diasohydrate melts at 175, is obtained non a-chloracetoacetic ester and thiourea. Its diasohydrate melts at 100° with decomposition. μ -Oxy.,3-methylthiazole Carboxylic Ester, $C_3(OH)(CH_3)SN \cdot COOC_2H_5$, melting at 128°, is formed from a-sulphocyanacetoacetic ester (A. 259, 284, 298). μ -Mercapto-3-methylthiazole Carboxylic Ester, $C_3(SH)(CH_3)SN \cdot COOC_2H_5$, melting at 141°, is formed from a chloracetoacetic ester and ammonium dithiocarbaminate (B. 26, R. 604).

Dihydrothiazoles or thiazolines are synthesized from (I) alkylen haloids, or β -haloid alkylamines and thioamides (B. 24, 783; 29, 2610):

$$CH_{2}.NH_{3}$$
 + NH_{3} $C.CH_{3}$ CH_{3} CH_{4} CH_{5} $C.CH_{3}$

(2) By the action of P_2S_5 upon acidyl- β -bromalkylamides (B. 26, 1328):

$$C_{6}H_{5}.C \nearrow O \xrightarrow{\text{NH-CH}_{2}} \xrightarrow{P_{5}S_{5}} C_{6}H_{5}.C \nearrow N \xrightarrow{\text{CH}_{2}} C_{1}H_{2}$$

The thiazolines are much more readily decomposed than the thiazoles. μ -Methyl Thiazoline, boiling at 145°, on evaporation with hydrochloric acid, becomes β -amidoethyl mercaptan. μ -Phenylthiazoline, boiling at 276°, is obtained from benzoyl- β -bromethylamide by the action of P_2S_3 . It yields benzoyl taurine when it is oxidized:

$$\begin{array}{c|c} CH_2-S \\ & \downarrow \\ CH_2-N \\ \end{array} C \cdot C_0H_0 \xrightarrow{O} \begin{array}{c} CH_2-SO_0H \\ & \downarrow \\ CH_2-NH-COC_0H_0 \end{array} (B. 23, 158).$$

a-Methyl- μ -tolylthiazoline, $C_3H_3(CH_3)(C_7H_7)NS$, boiling at 295°, is made from β -brompropyltolylamide and P_2S_5 . Thiazoline- μ -mercaptan, CH_2-S CSH, melting at 107°, is prepared from bromethylamine and S₂C (B. 22, 1152), as well as by the action of carbon bisulphide upon vinylamine, CH₂: CH.NH₂ (B. 28, 2932).

The alkylen derivatives of pseudosulphourea, previously discussed, are amidothiazolines. They have mostly been obtained by rearrangement of allyl thioureas (thiosinemines, 1, 409): μ-Anilido-a-methyl Thiazoline, n. Phenylpropylene-ψ-thiourea, C₃H₃-(CH₃)NS(NHC₆H₆), melting at 117°, is made from allyl phenylthiourea: CH₂ = CH HS:
CNHC₆H₆ (B. 22, 2991).

 μ -Piperyl-a-methyl Thiazoline, $C_3H_1(CH_3)NS(NC_3H_{10})$, boiling at 277°, is obtained from allylpiperylthiourea (B. 24, 265). μ -Methylamido- a_3 3-diphenylthiazoline, $C_2H_2(C_4H_5)_2NS(NHCH_2)$, melting at 155°, is derived from diphenyloxyethylamine (p. 372) and methyl mustard oil (B. 28, 1900).

The following are derivatives of tetrahydrothiazole:

 β_{μ} -Diketotetrahydrothiazole, or Mustard Oil Acetic Acid, $\stackrel{CH_3-S}{CO-NH}>CO$, melting at 112°. It results on evaporating sulphocyanacetic acid or sulphocyanacetmelting at 112. It leads to a said amide with acids (B. 26, R. 324; 1, 423).

CH₂—S

β_μ-Ketolmidotetrahydrothiazole, CO _ CH₂ C NH, melting at 71°, is formed in the action of concentrated sulphuric acid upon sulphocyanacetamide. β,μ -DiketoCOOH.CH,.CH—S

COOH.CH,.CH—S

C:NII, melting with decomposition at 169°, is formed from $\beta \mu$ -imidoketotetrahydrothiazole acetic acid, COOH. CH₃.CH—S OC __NH>C: NH, melting at 216°, which is the condensation product of chlorsuccinic acid and thiourea (B. 27, R. 742).

10. BENZOTHIAZOLES.

The benzothiazoles, the analogues of the benzimidazoles and benzoxazoles (anhydro-bases) are prepared (1) from o-amidothiophenols (p. 157) and carboxylic acids (their chlorides or anhydrides) by the exit of water (A. W. Hofmann, B. 13, 1224):

$$C_0H_4 <_{NH_2}^{SH} + COOHR \longrightarrow C_0H_4 <_N^S > C.R.$$

(2) Upon heating acid anilides with sulphur, or oxidizing thioanilides with potassium terricyanide:

$$C_gH_g$$
 —N C_gH_g — C_gH_g C_gH_g C_gH_g C_gH_g C_gH_g C_gH_g C_gH_g C_gH_g C_gH_g

Phenylbenzothiazole is also produced on heating benzylamine with sulphur. Hydro-ten sulphide is evolved and thiobenzanilide is first formed, which then reacts in the sense above indicated (A. 259, 300).

The benzothiazoles are feeble bases; their odor resembles that of quinoline. with caustic potash resolves them into amidothiophenols and carboxylic acids.

Different benzothiazole derivatives are important as substantive cotton dyes.

Benzothiazole, Methenyl amidothiophenol, C. H. (NSCH), boiling at 234°, is produced from o-amidothiophenol and formic acid, or formanilide and sulphur.

Benzisothiazole, $C_0H_4 < {CH \atop N} > S$, boiling at 242°, is isomeric with benzothiazole. It is formed in the reduction of the o-nitrobenzyl ester of carbaminthiolic acid or of o-nitrobenzylmercaptan (p. 180) (B. 28, 1028; 29, 160).
\$\mu\$-Methylbenzothiazole, C_H_4(NSC_2H_2), boils at 238°.
\$\mu\$-Phenylbenzothiazole melts at 114°.
\$\mu\$,p-Amidophenyl-toluthiazole, Dehydrothiotoluidine, CH₃. C₆H₃. NH₂. me¹.

ing at 191°, is produced when thiotoluidine is heated with sulphur. Its trincthylam-monium chloride derivative is the dye Thioflavin. Dehydrotoluidine, when further heated with thiotoluidine and sulphur, yields the base of the dye Primulin:

$$CH_3 \cdot C_4H_3 \stackrel{S}{\searrow} C \cdot C_4H_3 \stackrel{S}{\searrow} C \cdot C_4H_4NH_3.$$

A series of benzothiazole derivatives has been obtained from chlorphenyl-mustard oil, or μ -chlorbenzothiazole, $C_0H_4 < S$ CCI, melting at 24° and boiling at 248°. It results when PCls acts upon phenyl-mustard oil. The reduction of chlorphenyl-mustard oil leads to benzothiazole; with alcohol we get μ-oxybenzothiazole; with sodium ethylate, μ -ethoxybenzothiazole; with sodium sulphydrate, sulphydro-, with ammonia,

ethylate, \$\mu\$-ethoxybenzothiazole; with sodium sulphydrate, sulphydro-, with ammonia, amido-, and with aniline, anilido-benzothiazole. \$\mu\$-Oxybenzothiazole, \$C_tH_{\text{(NSC-Oth)}}\$ (NSC-Oth), melting at 136°, is formed from chlorcarbonic ester and amidothiophenol. \$\mu\$-Ethoxybenzothiazole, \$\text{cthoxy-mustard oil}\$, \$C_{\text{c}}H_{\text{d}}(NSCO_{\text{c}}H_{\text{d}})\$, melting at 25° and boiling above 360°, results upon oxidizing phenylthiomethane with potassium ferricyanide. \$\mu\$-Sulphydrobenzothiazole, \$C_{\text{c}}H_{\text{d}}(NSC.SH)\$, melting at 179°, is also obtained from amidothiophenol and \$CS_{\text{s}}\$; from zobenzene with \$CS_{\text{s}}\$; from phenyl-mustard oil and sulphur, etc. \$(B. 24, 1403)\$. \$\mu\$-Amiliobenzothiazole, \$C_{\text{d}}H_{\text{d}}(NSC.NH)\$, melting at 159°, is also formed from azobenzene and phenyl-mustard oil \$(B. 24, 1410)\$. Bisbenzothiazole, \$C_{\text{d}}H_{\text{d}}(\text{NSC}, \text{NHC}_{\text{d}})\$, is produced when sulphur is heated with acctanilide. is heated with acetanilide

The hypothetical nucleus of Selenazole, H = CH Se, corresponds to this cole. Some derivatives of it have been obtained in a manner similar to that used with the N = C(CH₃) Se, boiling analogous thiazole derivatives. μ -Methyl Selenazoline, $CH_2 - CH_3$ Se, boiling at 161°, results on treating di-acetamidoethyldiselenide, $(CH_3, CO, NH, CH_2, CH_3Se)$, with phosphorus pentachloride. It is an oil with an odor resembling that of pyridine (B. $NH = C(NH) \setminus Se,$ 25, 3048). μ -Imidotetrahydroselenazole, Ethylene- ψ -selenurea, $\stackrel{\text{NR}}{\downarrow}$ — $\stackrel{\text{C(NR)}}{\hookrightarrow}$ Se, is an oil. It is obtained from bromethylamine and potassium selenocyanide (B. 23, 1003). The ring-homologous trimethylene- ψ -selenurea, $\stackrel{\text{CH}}{\hookrightarrow}$ — $\stackrel{\text{NR}}{\hookrightarrow}$ — $\stackrel{\text{C(NR)}}{\hookrightarrow}$ is prepared in an analogous way.

II. OSOTRIAZOLES OR PYRRO-[aa,]-DIAZOLES.

Osotriazones (1, 328), pyrro-[aa₁]-diazoles, $\frac{CH}{CH} = \frac{N}{N}$ NH, derivatives of osotriazole, are formed:

1. By boiling with acids or distilling the osazones of o-diketo-compounds, or the osotetrazones, which are the oxidation products of the osazones:

$$\begin{array}{c} C_6H_5.C = N-NHC_6H_5 \\ C_6H_5.C = N-NHC_6H_5 \\ \end{array} \rightarrow \begin{array}{c} C_6H_5.C = N-NC_6H_6 \\ C_6H_5.C = N-NC_6H_5 \\ \end{array} \rightarrow \begin{array}{c} C_6H_5C = N \\ C_6H_5.C = N-NC_6H_5 \\ \end{array} \rightarrow \begin{array}{c} C_6H_5C = N \\ \end{array} \rightarrow$$

2. By the action of acetic anhydride or PCls upon the hydrazoximes of the o-diketocompounds; water is split off in this reaction (p. 124):

$$\begin{array}{c} C_{e}H_{5}-C=NNHC_{e}H_{5} \\ \downarrow \\ C_{e}H_{5}-C=NOH \end{array} \longrightarrow \begin{array}{c} C_{e}H_{5}C=N \\ \downarrow \\ C_{e}H_{5}C=N \end{array} \nearrow N \cdot C_{e}H_{5}.$$

The methyl phenylhydrazones of a-ketoximes also yield osotriazoles with the elimina-

Behavier: Osotriazoles are mostly feeble basic liquids with an odor resembling the alkaloids. They distil without decomposition. Their imide hydrogen can be replaced by metals. The phenyl group of the n-phenyltriazoles can be replaced. The phenyl group of the n-phenyltriazoles can be split off after amidation by simple oxidation. Potassium permanganate oxidizes c-alkylosotriazoles to osotriazole

Carboxylic acids. However, the osotriazole ring is stable toward most reagents.

Osotriazole, C₂H₂N₃, melting at 22° and boiling at 204°, is obtained from its carboxylic acid (see below). Silver nitrate precipitates osotriazole silver, C₂H₂N₃Ag, from its aqueous solution. Benzoyl chloride produces n-benzoyl osotriazole, melting at 100°. n-Phenylosotriazole, C₂H₂N₃. C₂H₃, boiling at 224°, is formed from its carboxylic acid or from glyoxal osotetrazone. n-Phenylmethylosotriazole, C₂H(CH₃)N₃. C₆H₅, boiling at 150° (60 mm.), is obtained from methyl glyoxal. n-Phenyldimethylosotriasole, C₂(CH₃)₂N₃. C₆H₅, boiling at 192° (60 mm.), is formed from dimethyl glyoxal (1, 328; 11, 124). Triphenylosotriasole, C₂(C₆H₅)₂N₃, melting at 122°, is obtained from benzil (B. 21, 2806).

n-Phenyl-c-amido-c-methylisotriazole, C₂(CH₃)(NH₂)N₃C₆H₅, melting at 83°, is formed from acetylamidrazonphenylhydrazone, C₆H₅NHN: C(NH₂). C(CH₃): N.-NHC₂H₅ (B. 26, 2783; 28, 1283). It forms a diazo-compound, which, on boiling with water, becomes n-phenylmethyl oxyosotriazole, C₂(CH₃)(OH)N₃C₆H₅, melting at

water, percomes n-pnenyimetnyi oxyosotriazole, $C_2(CH_3)(OH)N_3C_6H_5$, melting at 141°, and with potassio-copper cyanide it forms n-phenyimethylcyantriazole. n-Phenyldiamido-osotriazole, $C_2N_3(C_6H_5)(NH_3)_2$, melting at 143°, is derived from oxalenphenylhydrazide-amidoxime, $C_6H_5NH.N:C(NH_2)C(NH_3):NOH.$ In certain respects it shows great similarity to the aromatic o-diamines (p. 95), in that it forms an axine-like blue dyestuff; with o-diketones it yields quinoxaline-like bodies. It does not form anhydro-bases. Nitrous acid converts it into a stable diazo-compound, which is readily changed by sodium acetate to phenylosotriazole-azimide, N=C-NH.

 $C_8H_8N N = C - NH N$. The latter can be readily decomposed into the diazo-com-

pound (A. 295, 129).

n-Phenyltriazole Aldehyde, C₂H(CHO)N₃C₆H₅, melting at 70°, is obtained from its oxime, melting at 115°, which is formed from disonitrosoacetone phenylhydrazone, HON: CH. C = N. NHC₆H₆ (1, 479). By the exit of water the aldoxime becomes

CH = N.OH

n-phenylcyantriasole, C(CN)HN₂C₈H₅, melting at 94°.
Osotriazole Carboxylic Acid, C₂(COOH)HN₂H, melting at 211°, results in the oxidation of n-amidophenylosotriazole carboxylic acid with potassium permanganate. The latter acid is obtained by the amidation of n-phenylosotriazole carboxylic acid, C₂(COOH)HN₂C₂H₅, melting at 192°, the oxidation product of n-phenylmethyltriazole. Phenylosotriazole carboxylic acid, when reduced by sodium amalgam, is resolved into prussic acid and phenylhydrazido-acetic acid. n. Phenylosotriazole Dicarboxylic Acid, C₂(COOH), N₂C₂H₅, melting at 236°, from phenyldimethyltriazole, readily yields an anhydride, melting at 184°.

The pseudo-azimides may be viewed as benzo-derivatives of osotriazoles. A constitution similar to that given the indazoles has been ascribed to them, hence they may

be called indodiasoles:

$$C_0H_4 < \stackrel{CH}{\dot{N}} > NR$$
 $C_0H_4 < \stackrel{N}{\dot{N}} > NR$

Index places

Pseudoazimides.

Pseudoazimides are produced when o-amido-azo-compounds are oxidized (comp. B. 25, 901; 27, 2374, etc.). The condensation can also be effected by means of thionyl chloride (B. 28, 2201).

Should the amido-group be substituted the oxidation will give rise to amustine hydroxide compounds (B. 20, 1174; 28, 328).

Prepared from bases of the naphthalene series. This reaction can easily be made not gressive by reducing agents:

o-Anilidonaphthalene-azo-benzoic acid yields the acid of the latter compound. It readily changes to a betaine-like anhydride: $\begin{array}{c} C_6H_5 \\ C_{10}H_6 < \stackrel{\cdot}{N} > N \end{array}$. $\begin{array}{c} O \\ C_6H_4 \cdot \stackrel{\cdot}{CO} \end{array}$ (B. 28, 333)

12. PYRRO[ab]DIAZOLES:
$$N = N$$
NH.

The azimides, or benzopyrro[ab]diazoles, are isomeric with the pseudoaimides. The oxidation of azimidotoluene produces pyrro[ab]diazole dicarboxylic acid, which by the loss of CO₂ becomes azole, the constitution of which is proved by this method of formation (B. 26, 2736):

$$\begin{array}{c|c} CH_3, C_6H_3 & NH \\ N & \longrightarrow & COOH, C-NH \\ \hline \\ Azimido-toluene & Pyrrodiazole Dicarboxylic Acid & Pyrro[ab]diazole. \end{array}$$

Pyrro[ab]diazole boils at 209°; its benzoyi-derivative melts at 111°. Pyrro[ab]diazole Dicarboxylic Acid melts with decomposition at 200°. n-Phenylpyrro[ab]diazole Dicarboxylic Acid, C₁(CO(H)₂N₃C₆H₅, melting at 150°, is probably the acid, the exter (m. p. 127°) of which is produced when diazobenzene-imide acts upon actylene dicarboxylic ester (B. 26, R. 585):

This reaction is similar to that by which pyrazole carboxylic esters are formed from diazo-acetic with acetylene dicarboxylic esters (p. 485).

Consult J. pr. Ch. [2], 53, 341, for an n-oxypyrro[ab]diazole dicarboxylic acid.

Benzopyrro[ab]diazoles or azimide-benzenes result from the action of nitrous acid upon o-diamines (p. 96):

$$\begin{array}{c} C_6 H_4 \subset \stackrel{\text{NH}_2}{\text{NH}_2} \longrightarrow \left(C_6 H_4 < \stackrel{\text{N}}{\text{N}} \stackrel{\text{NOH}}{\text{N}} \right) \longrightarrow C_6 H_4 \subset \stackrel{\text{N}}{\text{N}} \searrow N \\ \text{o-Amidodiazobenzene} & \text{Azimidobenzene.} \end{array}$$

When the benzene nucleus is substituted the n-substituted azimidobenzenes occur in two isomeric forms, determined by the position of the NR-group with reference to the benzene substituents. This is a proof of the unsymmetrical structure of the azimidobenzenes. When, however, the NH-group is free there always appears to be but one preferred position of the hydrogen atom (see uramidozimidobenzoic acids, p. 212 and A 291, 313). The azoImidobenzenes no longer manifest the instability of the diazo of diazamido-derivatives, but can be distilled without decomposition. The imide hydrogen can be replaced by alkyls. The tertiary bases form ammonium bases with alkyl iodides.

i-Oxyderivatives of the azimido-benzenes, the Azimidoles, are formed when alkalies act pon o-nitrophenylhydrazines (B. 27, 3381; 29, R. 790):

$$C_{e}H_{4} \stackrel{NH-NH_{2}}{\longrightarrow} C_{e}H_{4} \stackrel{N(OH)}{\longrightarrow} N \text{ (or } C_{e}H_{4} \stackrel{NH-N}{\longrightarrow} 0$$
•-Nitrophenylhydrazine

Azimidole.

Asimido-benzene, C₆H₄(N₃H), melting at 98°, is isomeric with diazobenzene-imide 1211). [2]n-Phenylazimido[4]ethoxy-benzene melts at 108°. [2]n-Phenylazimido[5]ethoxy-benzene melts at 99° (compare J. pr. Ch. [2], 53, 97). n-Tolylatinido-toluene, C₇H₆(N₃. C₇H₇), melting at 95°, is derived from o-amidoditolylamine 23, 1623), and is isomeric with n-tolyl-ψ-azimido-toluene (p. 510), melting at 126°. Benzoazimidole, C₆H₆(N₃OH), melting at 157°, is formed in the action of alkalies active phenylhydrazine. It is a rather strong acid. It yields the iodethylate of active phenylhydrazine. It is a rather strong acid. It yields the iodethylate of active phenylhydrazine with ethyl iodide. Hydriodic acid reduces it to azimidobenzene, while potassium permanganate oxidizes it to a strong tribasic acid, probably n-oxypyrrolab]diazole dicarboxylic acid (see above).

13. TRIAZOLES.

The triasoles or pyrro-[ab₁]-diazoles, (3)CH = $\stackrel{(2)}{N}$ NH(1), are isomeric with osomeric and approach discoles. The symmetrical $\stackrel{(5)}{\sim}$ NH(1), are isomeric with osomeric and approach discoles.

tiasole and pyrro[ab]-diazole. The symmetrical formula of a pyrro-[bb₁]-diazole, N = CH NH, may be suggested for the simplest triazole; certain of the n-alkyl triasoles introduced here are derived from it. In behavior the triazoles recall the pyrazoles (n. 482).

Formation of Triasoles: (1) Cyantriazoles are formed when the anhydrides of fatty acids act upon dicyanphenylhydrazine or cyanamidrazone (B. 26, 2385). Aldehydes and betones react similarly (Bladin, B. 18, 1544; 25, 183):

$$\begin{array}{l} \textbf{CN.C} = \textbf{N-NHC}_{6}\textbf{H}_{5} \\ \textbf{j} \\ \textbf{NH}_{2} \\ \textbf{Dicyanphenylhydrazine} \\ + (\textbf{CH}_{3}\textbf{CO})_{2}\textbf{O} \rightarrow \begin{array}{c} \textbf{CN.C} = \textbf{N-NHC}_{6}\textbf{H}_{5} \\ \textbf{j} \\ \textbf{NH.CO.CH}_{3} \\ \textbf{NH.CO.CH}_{3} \\ \textbf{3-Cyan-5-methylphenyl-triangle} \\ \end{array}$$

Acetylcyanamidrazone is an intermediate product. It may be viewed as a monohydrazone of a β -diketone, the terminal CH₂-group of which has been replaced by NH; this renders the reaction parallel with that of the formation of the pyrazoles from the hydrazones of the β -diketones.

Other amidrasones or hydrasidines (p. 129) (B. 27, 3273)—e. g., phenylamidrazonemethyl ketone (B. 26, 2782), amidoguanidine (B. 26, 2598), benzoylbenzenylhydrazidine (B. 27, 989), etc.—react like cyanamidrazone.

(2) Acidylthiosemicarbazides of the general formula HS. C(NHR): N. NHCOR, when heated beyond their melting point, yield mercaptotriazoles, which change to triazoles upon oxidation. The resulting triazole derivatives, so far as they are formed from a-alkylic thiosemicarbazides, are derived from a pyrro[bb₁]diazole (see above) (B. 29, 2483):

(3) Triazoles result upon distilling triazolons and urazoles with P2Sx (see p. 481) (B. 25. 225; 27, R. 408):

$$\begin{array}{c}
CO-NH \longrightarrow \\
N = C \cdot CH_{5} \longrightarrow N \cdot C_{6}H_{5} \longrightarrow P_{5}S_{5} \longrightarrow N \longrightarrow C \cdot CH_{5} \longrightarrow NC_{6}H_{6} \\
Phenylmethyltriazolon \longrightarrow Phenylmethyltriazole.$$

The chlortriazoles formed by the action of PCls upon the triazolons can be reduced to

triazoles (below).

(4) The method of producing triazoles by the condensation of acid hydrazides with acid amides is very simple (B. 27, R. 801). The reaction can be further simplified by allowing one molecule of hydrazine hydrochloride to act upon two molecules of the acid amide; the acid hydrazide will be formed in the first phase (Gaz. chim. ital. 26, 11, 413):

$$\begin{array}{c} \text{HCO} \\ \mid \\ \text{NH}_2 \\ \text{Formamide} \end{array} + \begin{array}{c} \text{NH}_2 \cdot \text{NH} \cdot \text{CH} \\ \mid \\ \text{O} \\ \text{Formbydrazide} \end{array} \\ \begin{array}{c} \text{HC} = \text{N-NH-CH} \\ \mid \\ \text{NH}_2 \\ \text{O} \end{array} \\ \begin{array}{c} \text{CH} = \text{N} \\ \mid \\ \text{NH}_2 \\ \text{O} \end{array} \\ \begin{array}{c} \text{CH} = \text{N} \\ \mid \\ \text{NH}_2 \\ \text{O} \end{array} \\ \begin{array}{c} \text{CH} = \text{N} \\ \mid \\ \text{NH}_2 \\ \text{O} \end{array} \\ \begin{array}{c} \text{NH} \\ \mid \\ \text{Triazole.} \end{array}$$

Behavior: The triazoles, like the other pyrrodiazoles, are feebly basic, nearly neutral bodies. The platinum chloride double salts behave similarly to the pyrazoles (p. 481, Gaz. chim. ital. 26, 11, 417). The imide-hydrogen is replaceable by metals. c-Alkyltriazoles yield triazole carboxylic acids when they are oxidized. In the n-phenyl triazoles the phenyl group, particularly after amidation, is split off by oxidation (compare

n-phenyl pyrazoles, n-phenyl osotriazoles, pp. 483, 508).

Triazole, C,H₃N₃, melting at 121° and boiling at 260°, is obtained (1) from formamide and formhydrazide; (2) by distilling urazole with P2S5; (3) from its carboxylic acid; (4) in the oxidation of mercaptotriazole with hydrogen peroxide (B. 29, 2485). n-Methyl- and n-ethyl triazoles are similarly formed from the corresponding mercaptan derivatives. 3-Methyl Triazole, C₂H₂(CH₃)N₃, melting at 94°, is derived from n-phenyl-3-methyl triazole by elimination of the C₆H₅-group by the oxidation process (B. 25, 225). n-Phenyl Triazole, C₂H₂N₃C₆H₅, melting at 47° and boiling at 266°, is derived from its carboxylic acid. n-Phenyl-3-methyl Triazole, C₂H (CH₃)N₃C₆H₅, melting at 87° and boiling at 274°, results when P₃S₅ acts upon n-phenylmethyl triazole. The phenyl methyl triazole, melting at 87° and boiling at 274°, results when P₃S₅ acts upon n-phenylmethyl triazole. mening at 07° and bolling at 274° , results when F_3S_6 acts upon n-phenylmethyl triazolon. Isomeric 1,5-Phenyl methyl triazole, melting at 191° , is formed from its carboxylic acid. 1,5-Diphenyl triazole, melting at 91° , is produced when 1,5-phenyl-3-chlortriazole is heated to $150-160^{\circ}$ with phosphorus and hydriodic acid. c-Diphenyl Triazole, $C_2(C_6H_5)_2N_3II$, melting at 188° , is obtained from benzoylbenzenyl hydrazidine (p. 205). c-Difuryl Triazole, $C_2(C_4H_5O)_2N_3II$, melting at 185° , is formed when difurylhydrazidine, C_4H_5O . C NII_2 HN C. C_4H_3O , is boiled with glacial acetic

acid (B. 28, 465). 1,3,5-Triphenyl Triazole, melting at 104°, is produced in the condensation of phenylhydrazine with benzonitrile in the presence of sodium (B. 29, R.

1125). Chlortriazoles result on heating triazolons with PCIs and POCIs to elevated temperatures. The chlorine in them is intimately bound and can only be removed on heating with III + P. 1 Phenyl 5 chlortriazole melts at 54°. 1,5-Diphenyl-3-chlortriazole melts at 96°. 1 Phenyl-3,5-dichlortriazole melts at 94° (B. 29, 2671; C. 1897, 1,

Mercaptotriazoles, from acidylthiosemicarbazides (see method 2), yield disulphides by gentle oxidation. More energetic oxidation splits off sulphur, and triazoles result. Mercaptotriazole melts at 216°. n-Methyl and n-Ethyl Mercaptotriazole melt at 168° and 97° (B. 29, 2484).
5-Amido-3-methyl Triazole, C₂(NII₂)(CH₃)N₃H, melting at 148°, is obtained from

acetylamidoguanidine, NH₂. CNH NH₂ (B. 26, 2589). 3-Acetyl-1-phenyl-5-NH . CO. CH₃ (B. 26, 2589). methyl Triazole, C₂(COCH₃)(CH₃)N₃C₆H₅, melting at 89°, is derived from phenylamidrazon-methyl ketone (B. 26, 2787). 3-Cyan-1-phenyl-5-methyl Triazole, melting at 109°, is formed from dicyanphenylhydrazine (see above).

Triazole Carboxylic Acids: Triazole-3-carboxylic Acid, $C_2H_2(COOH)N_3$, melts with decomposition at 137°. It is produced in the oxidation of methyl triazole and when **EXAMPLY** acts upon n-amidophenyltriazole carboxylic acid. n-Phenyl triazole-3-carboxylic Acid, $C_3H(COOH)N_3$. C_6H_6 , melting at 184°, is derived from phenylmethyl Exiazole as well as by the exit of CO_3 from n-phenyltriazole-3,5-dicarboxylic acid, $C_3(CH_3)(COOH)N_3$. C_6H_6 , which is prepared by the oxidation of n-phenyl-5-methyl Exiazole-3-carboxylic acid, $C_3(CH_3)(COOH)N_3$. C_6H_6 , melting at 177°. The latter areasolts from the saponification of its nitrile, as well as by the moderated oxidation of meetylphenylmethyl triazole.

Bistriasoles are formed in the action of acids (and their anhydrides) upon cyanhydra-

zeine and -phenylhydrazine (B. 26, 2389) (B. 21, 3063; 30, 1194):

$$\begin{array}{c} \textbf{C_gH_g.NH-N} \\ \textbf{NH_2} \\ \textbf{Cyanphenylhydrazine} \end{array} + (\textbf{CH_3CO})_3 \textbf{O} \rightarrow \textbf{C_gH_5N} \\ \begin{array}{c} \textbf{N=C-C=N} \\ \textbf{C(CH_3)=N} \\ \textbf{N=C(CH_3)} \\ \textbf{N=C(CH_3)} \end{array} \\ \textbf{N.C_gH_5} \\ \textbf{Dis-phenylmethyl Triazole.} \end{array}$$

Bistriazole, (C₂H₂N₂)₂, from cyanhydrazine and formic acid, is a compound sub-**Eiming** above 300°

Hydrotriasole Derivatives: The triazolons are keto-derivatives of dihydrotriazoles. They can also be viewed as oxytriazoles (compare pyrazolons, p. 486, and C. 1897, II, 269). They are produced (1) by the interaction of acetyl methane and phenylhydramines (Andreocci, B. 22, R. 737):

$$CH_8$$
— CO
 NH — $COOR$ + NH_8 . NHC_8H_8 \longrightarrow CH_8 — $C = N$
 HN — CO
 NHC_8H_8 .

The reaction suggests the formation of phenylmethylpyrazolon from acetoacetic ester and phenylhydrazine. Acetyl urethane is acetoacetic ester in which the CH₂-group has been replaced by NH (see above).

I-Phenyl-5-triazolon, $C_6H_5N-N=CH-NH-CO$, melting at 183°, has been prepared from its carboxylic acid—I-phenyl-5-triazolon-3-carboxylic acid. The latter is produced when KMnO₄ acts upon I-phenyl-3-methyl-5-triazolon, melting at 167° and builing above 200° (R. ca. P. co.) and boiling above 300° (B. 24, R. 203).

With these 1,5-triazolons, isomeric 1,3-triazolons or oxytriazoles are produced (1) on digesting acid derivatives of phenylsemicarbazide with dilute alkali (B. 29, 1946):

$$C_0H_5N < COR \\ NH - CO \cdot NH_2 \longrightarrow C_0H_5N < CR = N \\ NH - CO$$

(2) By the condensation of phenylsemicarbazide with aromatic aldehydes in the presence of an oxidant (C. 1897, I, 809), which probably first changes the phenylsemicarbazide to phenylazocarbamide:

$$C_6H_5NH.NH.CONH_2 \longrightarrow C_6H_5N: N.CONH_2 + OCII.CII_3 \longrightarrow \begin{array}{c} C_6H_5N-NHCO \\ C_6H_5C = -\frac{1}{N} \end{array}$$

1-Phenyl-3-triazolon, C₆H₆N.NH.CO.N:CH or C₆H₅N.N:C(OH)N:CH, from phenylsemicarbazide and formic acid, sublimes and melts at very high temperatures.

from phenylsemicarbazide and formic acid, sublimes and melts at very high temperatures.

1.Phenyl-5-ethyl-, -propyl-, -isobutyl-3-triazolon melt at 192°, 160°, and 165°.

1.5-Diphenyl-3-triazolon, melting at 290°, is obtained from benzoylphenylsemicarbazide as well as from phenylsemicarbazide and benzaldehyde.

1.Phenyl-5-styrenyl-3-triazolon, C₄HN₂O(C₆H₅)(CH: CHC₆H₅), melting at 287°, is formed from cinnamylphenylsemicarbazide, or cinnamic aldehyde and phenylsemicarbazide.

The triazolons are converted into triazoles by distillation with P₂S₅, or, better, by conversion into chlortriazoles and the reduction of the latter (B. 29, 2671).

The uragoles are the diketo-derivatives of tetrahydrotrianole. They result on hesting urea and its derivatives—e.g., allophanic ester, bluret, etc.—with hydranine salts:

Urazole, 3,5-Diketetriaselidine, C,H,O,N, melting at 244°, is obtained from hydrazodicarbonamide, NH, CO. NH, NH, CO. NH, (A. 263, 16). Urazole is a strong monobasic acid. It yields triazole when distilled with P,S, I-Phenyl

Urazole, $C_8H_5N-NH-CO-NH-CO$, melting at 263°, is formed from ures and phenylhydrazine, from phenylsemicarbazido-carboxylic ester (B. 28, 829), as well as from phenylhydrazido-oxalhydroxamic acid, $H_2N-C-CONHNHC_8H_8$, by Beckmann's NOH

transposition (A. 205, 136). Methyl iodide converts it into dimethylphenylurank, melting at 90°. Isomeric 3-Phenylurasole, C₂H₂N — CO — NH — NH — CO, melting at 203°, is formed by the interaction of hydraso-dicarbonazaide and aniline hydrochloride (l. c.).

Thio- and imido-derivatives of urasole have been obtained from the corresponding

thioures- and guanidine-compounds of hydrazine (B. 29, 2506):

Thiourasole, NH. CS. NH. CO. NH, melting at 177°, is obtained from hydrasothio-dicarbonamide, NH, CS. NH. NH. CONH, Dithiourasole, NH, CS. NH, CS. NH, melting at 245° with decomposition, and imido-thiourasole, NH. CS. NH. C(NH).NH, melting at 222°, are formed simultaneously when strong hydrochloric acid acts upon hydrazodithiodicarbonamide (B. 29, 2506).

Diimidourazole, Guanazole, NH. C(NH). NH. C(NH). NH, melting at 206°, is obtained from hydrazine and dicyandiamide by the action of hydrazine (B. 27, R. 583):

14. FURAZANES OR FURO[44,]DIAZOLES.

The furazanes or azoxazoles, furo-[aa₁]-diazoles, $\stackrel{CH}{c} = \stackrel{N}{N} O$ (1, 483), correspond to the osotriazoles. Just as the latter are obtained from the osazones (p. 508), so furazanes are produced from the glyoximes, the dioximes of o-diketones, or their oxidation products, the glyoxime-peroxides (B. 28, 69), by the action of alkalies:

As we observed in connection with the isoxazoles, those furazane derivatives in which the H-atoms of both methine groups are substituted are stable bodies. If one of the groups is free, a rearrangement into nitriles of a-ketonic acid oximes may readily take place. The alkyl furazanes can be oxidized to furazane carboxylic acids.

Phenyl Furazane, $C_2H(C_2H_3)N_2O$, melting at 30°, is very volatile. It is formed when soda acts upon phenylglyoxime diacetate. Sodium hydroxide converts it readily into the oxime of benzoyl cyanide, $C_2H_3C = N$ $C_2H_3C = NOH$ (B. 24, 3503).

into the oxime of benzoyl cyanide,
$$HC = N \longrightarrow C_8H_8C = NOH$$
 (B. 24, 3503)

It is stable toward acids. Dimethyl Furazane, C2(CH3)2N2O, melting at -7 boiling at 156°, results when dimethyl glyoxime is heated with ammonia to 160boiling at 156°, results when dimethyl glyoxime is heated with ammonia to 160-Methyl Ethyl Furazane, $C_2(CII_3)(C_2II_5)N_2O$, boiling at 170°, is similarly obt from methyl ethyl glyoxime. Diphenyl Furazane, $C_2(C_6II_5)_2N_2O$, melting a (p. 373), rearranges itself by prolonged heating into isomeric dibenzenylazoxim below) (A. 264, 180). Dibenzoyl Furazane, $C_2(COC_6II_5)_2N_2O$, melting at 11 prepared from dibenzoylglyoxime peroxide (B. 26, 529) (p. 381).

Furazane Carboxylic Acid, $C_2H(COOH)N_2O$, melting at 107°, on oxic becomes furazane propionic acid, the anhydride of dioxiniidovaleric acid (1, Methyl Furazane Carboxylic Acid, $C_2(CH_3)(COOH)N_2O(+H_2O)$, melting at 178° decomposition, are formed when potassium permanganate acts upon dimethylfura The dicarboxylic, like the monocarboxylic acid, is easily converted by boiling wate

The dicarboxylic, like the monocarboxylic acid, is easily converted by boiling wate

cyanimidoacetic acid.

-0.

Consult B. 28, 723, vol. 1, 500, for oxyfurazane carboxylic acid. Benzo-, naphtho-, phenanthro-furazanes, etc., have been prepared fror o-dioximes of the benzene, naphthalene, and phenanthrene series (see also B. 2 790).

15. AZOXIMES OR FURO[ab,]DIAZOLES.

The azoximes, $furo[a,b_1]$ diasoles, N - CH > 0, correspond to the triazoles or [ab₁]diazoles, and just as they are obtained from the amidrazones (p. 511), s azoximes are prepared:

I. From amidoximes and carboxylic acids (their chlorides or anhydrides):

$$\begin{array}{c} \text{CH}_{\text{3}} \cdot \text{C} = \text{NOH} \\ \text{j} \\ \text{NH}_{\text{2}} \\ \text{Ethenyl Amidoxime} \end{array} + \begin{array}{c} \text{CH}_{\text{5}} \cdot \text{C} = \text{N} \\ \text{j} \\ \text{N} = \text{C} \cdot \text{C}_{\text{6}} \text{H}_{\text{5}} \\ \text{Ethenylbenzenyl Amidoxime}. \end{array}$$

The amidoximes combine with the aldehydes of the fatty series to form hydrazo: which part readily with hydrogen and become azoximes. COCl₂ and CSCl₂ forn bonylazoximes (furo[ab1]diazolons) and acoximthiocarbinols (B. 19, 1487; 22,

2. Azoximes are also prepared by Beckmann's transposition from glyoximes c azanes (p. 381) (B. 27, R. 800):

$$\begin{array}{c} \textbf{C_gH_5. C = NOH} \\ \textbf{C_gH_5. C = NOH} \\ \textbf{Benzil Dioxime} \end{array} \\ \begin{array}{c} \textbf{C_gH_5-C = NOH} \\ \textbf{NH-CO. C_gH_5} \\ \end{array} \\ \begin{array}{c} \textbf{C_gH_5C = N} \\ \textbf{N = C. C_gH_5} \\ \textbf{Dibenzenyl Azoxime.} \end{array}$$

Diethenyl Azoxime, $C_3(CH_3)$, N_3O (B. 17, 2755), is a very volatile body. Etl Benzenyl Azoxime, $C_3(CH_3)(C_2H_3)N_3O$, melts at 41°. Dibenzenyl Azox $C_3(C_2H_3)_2N_3O$, melting at 108° and boiling at 290°, also results when hydroxylamin upon benzoyl benzimide chloride (A. 296, 284). Oxalenbisazoximethenyl, O < N = C - C = N $C(CH_s) = N$ $N = C(CH_s) > 0$, melts at 165° (B. 22, 2949).

Benzenyl Carbonyl Azoxime,
$$C_8H_6C = N > 0$$
, melting at 198°, and zenylazozim - thiocarbinol, $N = C(SII) > 0$, melting at 131°, are profrom benzenylamidoxime by means of COCl, and CSCl.

16. OXYBIAZOLES OR FURO[bb,]DIAZOLES.

Hypothetical oxybiazole, or fure $[b,b_1]$ discrete, N = CH > 0, yields—

Diphenyloxybiazole, *Dibensenyl Issaexime*, N₂C₂(C₂H₂)₂O, melting at 140°, which is isomeric with dibensenylasoxime and diphenyl farazane. It is prepared, like them, from benzil dioxime (A. 252, 60):

$$\begin{array}{c} C_gH_gC=NOH \\ C_gH_gC=NOH \\ \text{\tiny e-Benzil Dioxisse} \end{array} \rightarrow \begin{array}{c} N=C(C_gH_g)CI \\ N=C(C_gH_g)CI \end{array} \rightarrow \begin{array}{c} N=C(C_gH_g) \\ N=C(C_gH_g)CI \end{array} \rightarrow \begin{array}{c} N=C(C_gH_g) \\ N=C(C_gH_g)CI \end{array}$$

Furthermore, it also results when nitrous acid acts upon dibensenylhydrasidine (p. 205) (B. 27, 984):

$$\begin{array}{ll} N = C(C_0H_5)NH_2 & N_0O_0 \\ N = C(C_0H_5)NH_2 & N = C(C_0H_5) \\ \end{array} > O(+2N_0+2H_0O).$$

Ditolyloxybiasole, N₂C₃(C₁H₂)₂O, melting at 234°, is formed from ditolenylhydrizidine (B. 27, 3288).

The Keto-, thio-, or imido-oxybiazolines are derivatives of dihydro-oxybiazole or oxybiazoline. They are produced from carboxylic and urea derivatives of phenylhydrazine, naphthyl hydrazine, etc. (pp. 126, 127), through the action of phosgene, COCl, thiophosgene, CSCl₂, and phenyl isocyanogen chloride, CCl₂: NC₆H₆ (B. 23, 2843; 24, 4178; 26, 2870):

(2) $C_{10}H_1NH$ NH. CO. NH.

Naphthyl Semicarbazide

CIA C. NA.

Naphthyl Semicarbazide

CIA C. NA.

Naphthylamidothio-oxybiazoline, m. p. 2180

(3)
$$C_8H_5$$
. NH

$$NH . CHO + CCl_2 : N . C_8H_6 \longrightarrow C_8H_8N - C : (NC_8H_5)$$

$$N = CH$$

$$N = CH$$

$$n-Phenyl-phenyllmido-oxybiazolon, m. p. 99°.$$

17. The ring of furo[ab] diazole, | N, is only found condensed with benzene or naphthalene nuclei in diazo-oxides:

Dichlor-o-diazophenol, $C_0H_2Cl_2 \stackrel{O}{\searrow} N$, is formed by the action of N_2O_3 upon dichlor-o-amidophenol. Nitro-o-diazophenol, $C_0H_3(NO_3) \stackrel{O}{\searrow} N$, from p-nitro-o-amidophenol, deflagrates at 100° (B. 2, 52; A. 113, 212).

Naphthalene-2, I-diazo-oxide, $C_{10}H_6$ $\left\{ \begin{array}{c} [2]N \\ [1]O \end{array} \right\}$ N, melting at 76°, results upon oxidizing an alkaline naphthalene solution with potassium ferricyanide solution. 6-Nitronaphthalene-2, I-diazo-oxide, $C_{10}H_6(NO_3)(N_2O)$, from 6,2-dinitro-I-diazonaphthalene, is a substance exploding at 145° (B. 27, 680, 2214).

The thiodiazole-ring derivatives, corresponding to azoximes, oxybiazoles, and diazo-oxides, which contain furodiazole rings, occur in the groups of the executationes, this

biazoles, and diazosulphides. Piazthielen is a thiodiazole ring analogous to the fi ring.

18. Azosulphimes, or Thio[ab₁]diazoles: $\stackrel{CH = -N}{N} > S$, result from the ac carbon disulphide upon amidoximes (B. 24, 388):

$$\begin{array}{c} C_{e}H_{g}C=N.OH \\ \downarrow \\ NH_{g} \end{array} + CS_{g} \xrightarrow{C_{e}H_{g}C=N} \\ N=C(SH) \\ S=C(SH) \\ S=C(SH)$$

Azosulphime anilides are formed when phenyl mustard oil is used. Dibenzenyl Azosulphime, $C_0H_3C=N$ $N=C(C_0H_8)$ S, results from the action of upon thiobenzamide (B. 25, 1586).

19. The thiobiazolines are derivatives of thio[bb₁]diazole, N = CH > S. T sult from the action of aldehydes upon phenylsulphocarbazinic acid (p. 126), or, their ethers (B. 28, 2635):

The thiobiazoline sulphydrates formed in this manner are very acid. They are toward acids. Aqueous alkalies decompose them. They oxidize quite easily to See l. c. for the rearrangement of the latter (B. 29, 2127).

Amido-derivatives of the thiobiazolines are prepared from the thiosemicarbazid aldehydes (B. 30, 849):

$$\begin{array}{c} C_eH_bNH \\ N = C(NHC_eH_g) \\ Dipbenylthiosemicarbaside \end{array} + OCH \cdot C_eH_5 \longrightarrow \begin{array}{c} C_eH_bN - CH(C_eH_g) \\ N = C(NHC_eH_g) \\ Anilidophenylthiobiazoline, m. p. 1 \\ \end{array}$$

(1) Imidothiobiazolines, (2) ketothiobiazolines or pseudothiobiazolons, and (3) biasolines are made by the action of carboxylic acids, COCl, and CS, upon thiour dithio-carbamic acid derivatives of the hydrazines (p. 126; 24, 4190; 27, 613, 29, 2483):

Imidothiobiazoline, S. C(NH). NH. N: CII, melting at 191°, is obtaine formylthiosemicarbazide (B. 29, 2511). It is remarkable that the acidylthiosem zides, when deprived of water by acetyl chloride, yield thiobiazolines, but when above their melting point, mercaptotriazoles result:

(2)
$$C_{10}H_1NH$$
 $NH - CS . NH_2 + COCl_2 \longrightarrow C_{10}H_1N - CO$
 $N = C(NH_2)$

Naphthylaulphosemicarbazide

 $N = C(NH_2)$
 $N = C(SH_2)$
 $N = C(SH_2)$

n-Phenyldithiobiazoline Sulphydrate m. p. 910.

20. The addition product of phenyl mustard oil with discounthane may be viewed as a derivative of Thio[ab]diazole:

$$CH = CH$$

$$N = CH = C(NHC_0H_0)$$

$$N = N$$

$$N = N$$

$$N = N$$

$$N = N$$

a-Anilidothio[ab]diazole melts at 172° with decomposition. The acetyl derivative melts at 162°; the nitroso-derivative melts at 98° (B. 29, 2588).

The phenylene diazosulphides are beaso-derivatives of thio[ab]diazole. They correspond to the diazo-oxides and azolmides. They are produced when nitrous acid acts upon o-amidothiophenols:

The diazosulphides are more stable than the diazo-oxides. They resemble the azo-imides more particularly, as they only give up their nitrogen at higher temperatures, and then without deflagration. In doing this they yield diphenylene disulphides:

 $C_6H_4 < S > C_6H_4$. The diazosulphides are feeble bases and take up alkyl iodides (A. 277, 214).

Phenylene Diazosulphide, C_aH₁N₂S, melts at 35° and boils at 129° (10 mm.). Cumylene Diazosulphide, C_aH(CH₂)₂N₂S, melts at 85°.

21. The ring of thio[aa₁]diazole, C N S, unites with the benzene nucleus to form

Piazthioles, which also result upon treating the o-phenylenediamines with sulphurous acid (B. 22, 2895):

$$\begin{array}{c} CH = CH - C - NH_{2} \\ \downarrow & \downarrow \\ CH = CH - C - NH_{2} \\ o - Phenylene Diamine \end{array} + \begin{array}{c} SO_{2} \longrightarrow \begin{array}{c} CH = CH - C - N \\ \downarrow & \downarrow \\ CH = CH - C - N \\ \end{array}$$

The piazthioles are feebly basic bodies, which are very stable toward oxidants. The o-diamines result from their reduction.

The piaselenoles correspond to the piazthioles. They are similarly formed from o-diamines and selenious acid. In their stability they resemble the piazthioles.

Piaselenol,
$$C_6H_4 < N > Se$$
, melts at 76°.

Tolupiaselenol, C₇H₆(N₂Se), melts at 73° and boils at 267°.

22. Thio[abb₁]triazoles, or Triazsulpholes, N = NS: A series of compounds may be referred to this ring. They result from the action of nitrous acid upon thiosemicarbazide and alkylic thiosemicarbazides, whereas phenylthiosemicarbazide yields a tetrazole compound (B. 29, 2491):

$$CH_3. NH. \subset \stackrel{N-NH_2}{SH} + NOOH \longrightarrow CH_3. NH. C \subset \stackrel{N-N}{S-N}$$

The amidotriazsulpholes formed in this manner decompose, when boiled with water, into sulphur, nitrogen, and cyanamides, while with concentrated hydrochloric acid they yield nitrogen and thiocyanamides:

Methylamido-, ethylamido-, and allylamido-triazsulpholes melt at 96°, 67°, and 54°. Amido-triaz sulphole, from thiosemicarbazide and N₂O₂, deflagrates at 128–130°.

23. TETRAZOLES.

Two isomeric series of tetrazoles are possible. They can be distinguished as Pyrro- $\begin{array}{c} \text{CH} = N \\ \text{CH} = N \\ \text{NH}, \text{ and } pyrro[abb_1] triazoles, } \\ N = N \\ \text{NH}. \end{array}$ The syntheses do not invariably afford a certain basis for the judgment of the constitution of the tetrazoles (B. 29, 1846).

Tetrazoles are produced:

I. By the action of nitrous acid upon hydrazidines (amidrazones) (p. 205)—e. g., benzenylhydrazine (B. 27, 995), dicyanphenylhydrazine (Bladin, B. 19, 2598), amidoguanidine (A. 273, 144). This is similar to the formation of triazoles from the same compounds with carboxylic acids:

$$\begin{array}{c} \text{CN.C} = \text{N-NHC}_6\text{H}_5 \\ \text{N} \text{H}_2 \\ \text{Dicyanphenylhydrazine} \\ \end{array} + \text{N}_2\text{O}_3 \longrightarrow \begin{array}{c} \text{CN.C} = \text{N} \\ \text{N} = \text{N} \\ \text{N-Phenyl-3-cyantetrazole.} \end{array}$$

A tetrazole derivative which might be derived from pyrro[abb,]triazole is produced in the action of N₂O₂ upon phenylthiosemicarbazide (B. 28, 74):

$$\begin{array}{c} S:C-NH-NH_2\\ \downarrow\\ NHC_0H_5\\ \end{array} + N_2O_3 \longrightarrow \begin{array}{c} S:C-NH\\ \downarrow\\ C_0H_5N-N\\ n-Phenyl-5-thiotetrazcline. \end{array}$$

However, when nitrous acid acts upon diphenylthiosemicarbazide, sulphur is split off, and Diphenylisotetrazolon is produced:

$$SC <_{NH}^{NHC_0H_6} \xrightarrow{N_2O_6} CO <_{N - NC_0H_5}^{N(C_0H_5) - N}$$

It consists of red needles, melting at 110°. It is basic. Reduction causes it to break down again into diphenylsemicarbazide, and recalls the pseudo-azimides (p. 509) (B. 29,

1689).

2. With nitrous acid the amidines yield dioxytetrazotic acids. These, on reduction,

The latter are identical with the tetrazoles which are formed by the first method (A. 263, 101; B. 27, 994):

$$\begin{array}{c|c} \textbf{C_gH_5}. \ \textbf{C} = \textbf{NH} & & \textbf{N_fO_3} \\ \textbf{I} & & \textbf{N_fO_3} \\ \textbf{NH_5} & & \textbf{N} = \textbf{N} \cdot \textbf{OH} \\ \textbf{Benzenyl Amidine} & & \textbf{Dioxytetrazotic Acid} & & \textbf{H} & \textbf{C_6H_5C} = \textbf{N} \\ \textbf{N} = \textbf{N} \cdot \textbf{OH} & & \textbf{N} = \textbf{N} \\ \textbf{Dioxytetrazotic Acid} & & \textbf{Benzenyl Tetrazotic Acid, c-Phenyl Tetrazolc.} \end{array}$$

3. Finally, the tetrazoles are prepared by oxidizing suitable tetrazolium compounds,

Behavior: The tetrazoles are prepared by Oxidizing Suitable tetrazolum compounds, the oxidation products of formazyl derivatives (see below and p. 131).

Behavior: The tetrazole ring, composed of four N-atoms and one C-atom, shows in general equal stability with azole and pyrrol, containing less nitrogen. Thus, the n-phenylated derivatives, just as with the pyrazoles and the triazoles, can be converted by nitration into nitrophenyltetrazoles, and the amido-bodies from these may be oxidized to tetrazoles. The feebly basic character of pyrrol becomes in tetrazole a strong acid, the total influence of the Nature. due to the influence of the N-atoms. After comparing pyrrol in many respects with phenol, tetrazole may be arranged side by side with trinitrophenol. The silver and copper salts deflagrate violently on heating.

CH = N
Tetrasole, | NH, melting at 156°, sublimes and is prepared by treating diazotetrazole (see below) with alcohol (A. 287, 243); by oxidizing amidophenyltetrazole carboxylic acid (B. 25, 1412), as well as in the action of KMnO, upon di-p-oxydiphenyltetrazolium betaine (below). Sodium salt, CN4HNa + H2O; barium salt, (CN4H)2-Ba + 3½ H₂(). Tetrazole is decomposed into CO₂, N₂, and 2NH₂ when it is heated

with concentrated hydrochloric acid.

c-Phenyl Tetrazole, Benzenyl Tetrasotic Acid, C(CaHa)N4H, melts with decomposition at 219° (A. 263, 107). It is obtained from dioxytetrazotic acid or from benzenyl hydrazidine. c-Tolyl- and c-Furyl Tetrazolea, melting with decomposition at 234° and 199° respectively, are similarly formed from tolyl- and furylhydrazine (B. 28, 465). n-Phenyl Tetrazole, CHN₄. C₆H₅, from its acid, is an oil, deflagrating when heated.

Diphenyl Tetrazole, CN₄(C₈H₅)₂, melting at 107°, results when p-oxyphenyl diphenyltetrazolium hydroxide is acted upon with potassium permanganate, as well as in the oxidation of guanazyl benzene, C_6H_6 CN: $N : N(C_8H_6)$, with N_2O_3 or nitric acid.

It is characterized by its great stability (B. 29, 1854).

Bistetrazole, (CIIN₄), (?), is formed when N₂O₃ acts upon the addition product of cyanogen and hydrazine (B. 26, R. 891).

c-Amidotetrazole, Amidotetrazotic Acid, C(NH2)N4H, melting at 203°, results when nitrous acid acts upon diazoguanidine nitrate, and by further action of the acid yields diazotetrazole, which explodes in concentrated aqueous solution, even at oo. It

probably has the following constitution: C = N - N. Metallic oxides form stable salts N = N

with it. Their formula is C(N: N.OMe)N₄Me.

Tetrazyl Hydrazine, C(NHNH₂)N₄H, is produced by the reduction of diazotetrarole. It melts with decomposition at 199°. Nitrous acid converts it into tetrazylazoimide, C(N₃)N₄H, a beautiful crystalline, exceedingly explosive substance (A. 287, 238).

n Phenyl Tetrazole Carboxylic Acid, C(COOH)N₄C₆H₈, melting at 138°, results upon saponifying synthetic n-phenylcyantetrazole (see above).

Derivatives of pyrro-[abb₁]-triasole:

1-Phenyl 5-thiotetrazoline, $S: \stackrel{.}{C} - NH - N = N - \stackrel{.}{N} \cdot C_6H_5$ (?), melting with decomposition at 142-145°, is formed from phenylthiosemicarbazide when acted upon with nitrous acid. Digestion with caustic soda converts it into isomeric phenyltetrazole

mercaptan, HS. $\dot{C} = N - N = N - \dot{N}$. C_aH_b , melting at 150°. Both compounds yield the same silver salt, which methyl iodide converts into n-phenyltetrasolemethyl sulphide. Potassium permanganate produces n-phenyltetrazole sulphonic acid, C(SO₃H)N₄C₈H₃, which, upon heating with hydrochloric acid, splits off the sulpho-group and becomes

1 phenyl-5-oxytetrazole, OH . C = N - N = N - NC_BH_B, melting at 186°.

Tetrazolium compounds are those which result from the oxidation of formazyl bodies in a manner similar to that by which the azoammonium derivatives are obtained from the o anilido bodies (B. 27, 2920), and the osotetrazones from the osazones (p. 508).

$$\begin{array}{c} \text{HC} = \text{N-NIIC}_6\text{II}_5 \\ \text{N} = \text{N-C}_6\text{H}_5 \end{array} \xrightarrow{O} \begin{array}{c} \text{HC} = \text{N} \\ \text{N} = \text{N} \end{array} \begin{array}{c} \text{NC}_6\text{H}_5 \\ \text{OH } \text{C}_6\text{H}_5 \end{array}$$

$$\text{OH } \text{C}_6\text{H}_5$$

$$\text{n-Diphenyltetrazolium} \\ \text{Hydroxide.} \end{array}$$

The oxidation is best effected by amyl nitrite and hydrochloric acid. The tetrazolium hydroxides are, like all ammonium hydroxides, strong bases. Ammonium sulphide reduces them to formazyl compounds.

n-Diphenyl Tetrazolium Chloride, $CHN_4(C_6H_5)_2Cl$, melting with decomposition at 268°, results by the elimination of carbon dioxide from diphenyltetrazolium

PYRONES. 52I

chloride carboxylic acid, melting at 257° with decomposition. The ester of this acid is prepared from formazyl carboxylic ester (p. 129), and passes just as readily as the

p.-Dioxydiphenyl-tetrazolium Betaine, formed in an analogous manner, melts at 1796 with decomposition, and can be oxidized to tetrazole (B. 28, 1693):

$$\begin{array}{c}
(N-N, C_0H_4OH \\
N=N, C_0H_4, OH
\end{array}) \longrightarrow HC \begin{pmatrix}
N-NH \\
N=N
\end{pmatrix},$$

which demonstrates the connection between the tetrazoles and tetrazolium compounds. Similarly, p-monoxyphenyldiphenyltetrazolium chloride yields diphenyltetrazole (B.

29, 1852). Cyclodiphenyltetrazolium chloride carboxylic ester,

CO₂R. CV_N = N - C₄H₄, is derived from cycloformazyl carboxylic ester (p. 339; A.

N = NCl - C₄H₄

4. SIX-MEMBERED HETEROCYCLIC COMPOUNDS.

A. MONOHETEROATOMIC SIX-MEMBERED RINGS.

I. SIX-MEMBERED RINGS WITH AN O-MEMBER.

A series of cyclic bodies belongs here. They have already been discussed, according to their character, either with the fatty bodies or fatty aromatic substances with open chain, with which they are genetically related. They are the anhydrides of e-glycols (1, 300), the \delta-lactones,—
e. g., \delta-valerolactone (1, 345),—the anhydrides of the glutaric acids (1, 452), etc.:

These are unsaturated 8-lactones and acid anhydrides corresponding to the saturated 6-lactones and 8-acid anhydrides. Anhydrides of unsaturated e-glycols are not known, but there are anhydrides of diolefine dioxyketones. They are the r-pyrones, which are isomeric with the diolefine-**8-oxy-acid lactones**, the a-pyrones:

The pyrones and allied compounds are characterized by the fact that II--44

when they are digested with ammonia the linking oxygen atom is replaced by NH, and pyridones or oxypyridines (p. 534) result:

$$C(CO_2H) = CH$$

$$CH - CO$$
a-Pyrone Carboxylic Acid,
$$CO < CH = C(CH_2)$$

$$CH - CO$$

$$CH - CO$$

$$CH - C(CH_3)$$

$$CO < CH = C(CH_3)$$

$$CH - CO$$

$$CH - C(CH_3)$$

$$CO < CH - C(CH_3)$$

$$CH - C(CH_3)$$

$$CO < CH - C(CH_3)$$

$$CH - C($$

a. The coumalins belong to the a-pyrones:

a Pyrone, Coumalin, C₅H₄O₂, and 2,4-Dimethyl-a-pyrone, dimethyl coumalin,

C₅II₁(CII₂)₂O₂ (1, 362), are obtained from their acids:
Cournalic Acid, C₅H₃O₂. CO₂II, made by the action of concentrated sulphurk acid upon malic acid, and

Dimethyl Coumalic Acid, isodehydracetic acid, C₈H(CH₂)₂O₂. COOH, which is

produced by the action of sulphuric acid upon acetoacetic ester (1, 496).

Phenyl Coumalin, 1-Phenyl-a-pyrone, C₂H₂(C₂H₃)O₂, melting at 68°, occurs in the coto-bark.

d-Phenylvaleric acid results from its reduction. It yields a-phenylypidine with ammonium acetate (B. 29, 1673, 2659).

a, y-Pyronon yields: Dehydracetic Acid, or I-Aceto-3-methyl pyronon, C,H,

(CH₃)(COCH₃)(), (I, 52I), resulting upon boiling acetoacetic ester, and

Dehydracetcarboxylic Acid, I-Aceto-3-methylpyronon-2-carboxylic Acid, which is formed by the interaction of acetone dicarboxylic acid and acetic anhydride (1, 501, 521).

b. \(\gamma\)-Pyrones are uniformly produced by splitting off water from 1,3,5-triketones (B. 24, 111):

$$CO \stackrel{\text{CII}_2. \text{ CO . CO}_2\text{R}}{\stackrel{\text{COI}_2. \text{ CO . CO}_2\text{R}}{\stackrel{\text{CO}_2\text{R}}{\text{CH} = \text{C} \text{-CO}_2\text{R}}}} \rightarrow CO \stackrel{\text{CH} = \text{C} \text{-CO}_2\text{R}}{\stackrel{\text{CH} = \text{C} \text{-CO}_2\text{R}}{\text{Chelidonic Ester}}}$$

Conversely, they are readily reconverted into triketones. Although the pyrones contain a ketone oxygen atom, they do not react with hydroxylamine, etc.; compare the xanthones, p. 524.

? Pyrone, Pyrocomane, C₆H₂O₂, is formed when comanic and chelidonic acids are

heated. Carbon dioxide is eliminated. It melts at 32.5° and boils at 315°. a_1a_1 -Dimethyl Pyrone, $C_6H_2O_2(CH_3)_9$, results upon heating dehydracetic acid with hydriodic acid, or when carbon dioxide is expelled from its acid (A. 257, 253). It melts at 132° and boils at 248°. It sublimes at 80°. Boiling baryta-water converts it, with rupture of the ring, into diacetylacetone (compare dimethyl furfurane), which ammonia changes to lutidone.

Oxypyrone, C₅H₅O₂(OH), pyrocomenic acid, pyromeconic acid, is obtained from comenic and meconic acids by distillation. It melts at 121° and boils at 228°. It forms

unstable salts with bases.

Pyrone Carboxylic Acid, Comanic Acid, C₅H₃O₃. CO₃H, is obtained from chelidonic acid by the loss of carbon dioxide. It dissolves with difficulty in water. It melts at 250° and decomposes. When boiled with lime it decomposes into acetone, oxalic

acid, and formic acid. It forms an oxypicolinic acid when digested with ammonia.

Pyrone Dicarboxylic Acid, Chelidonic Acid, C₅H₃O₂(CO₂H)₃, melts at 220°, and occurs, together with malic acid, in *Chelidonium majus* (A. 57, 274). It can be readily obtained through the exit of water from acetone-dioxalic acid. It forms colorless salts. An excess of alkali converts it into salts of acetone-dioxalic acid or xanthochelidonic acid, which are yellow-colored.

The reduction of chelidonic acid gives rise to acetone-diacetic acid or hydro-chelidonic acid, and normal pimelic acid. Ammonia converts it into an oxy-pyridine dicarboxylic acid (p. 537).

Oxy-pyrone Carboxylic Acid, Comenic Acid, $C_5H_2(OH)(COOH)O_2$, from meconic acid, is converted by ammonia into dioxypicolinic or comenamic acid (p. 538), which can also be obtained from Meconic Acid, $C_5H(OH)(COOH)_2O_2 + 3H_2O$, which occurs in opium in union with morphine (A. 83, 352). It readily parts with carbon dioxide. Ferric salts color its solutions dark red.

Dimethyl Pyrone Dicarboxylic Acid, C₅(CH₂)₂(COOH)₂O₂; its diethyl ester, melting at 80°, is formed by the exit of water from carbonyl diacetoacetic ester, CO[CH(CO₂R)COCH₂]₂ (B. 20, 154; also B. 24, R. 573).

Tetrahydropyrone derivatives result from the condensation of acetone dicarboxylic esters and aldehydes by means of hydrochloric acid (B. 29, 994, 2051):

$$\text{CO} < \overset{\text{CH}_{3}(\text{CO}_{3}R)}{\text{CH}_{3}(\text{CO}_{2}R)} + 2\text{OCH.CH}_{3} \xrightarrow{\hspace*{1cm}} \text{CO} < \overset{\text{CH}(\text{CO}_{3}R) - \text{CH}(\text{C}_{6}H_{3})}{\text{CH}(\text{C}_{9}H_{3})} > 0.$$

Dimethyl- and diphenyl-tetrahydropyrone dicarboxylic diethyl esters melt at 102° and 115°. Similarly, diphenyldimethyl tetrahydropyrone, C₆H₆O₂(CH₈)₂, (C₆H₆)₃, melting at 106° and boiling at 236° (20 mm.), is formed from diethyl ketone and two molecules of benzaldehyde in the presence of alcoholic potash (B. 29, 1352).

The coumarins and isocoumarins are benzo-derivatives of a-pyrone:

$$C_{g}H_{4}\begin{cases} [1]CH = CH \\ [2]O \longrightarrow CO \\ (a-) & Benzopyrone, \\ (a-) & Comparin \\ (a-) & Benzopyrone, \\ (a-) & Be$$

The latter are more easily converted by ammonia into benzopyridone or oxyisoquinoline derivatives than the pyrones into pyridones.

Coumarin and its homologues have been discussed as lactones of o-oxycinnamic acids immediately after the latter (p. 280). Isocommarins, the lactones of benzene carboxylic acids, with hydroxylated side-chain unsaturated in the β -position, isomeric with the o-oxycinnamic acids, are produced by the following general methods:

I. Benzal-, xylal-, and alkylidene phthalides can be rearranged into isobenzalphthalides or isocoumarins (B. 20, 2363; 24, 3973):

$$\begin{array}{c} C = CH \cdot C_6H_5 \\ C_0 > O \\ CO \end{array} \longrightarrow \begin{array}{c} CH = CC_6H_5 \\ CO = O \\ \\ CO = O \end{array}$$
Benzalphthalide
Isobenzalphthalide, Phenylisocoumarin

When acid anhydrides or chlorides act upon o-cyanbenzyl cyanide, condensation products result which, upon treatment with acids, have one cyanogen group split off and the other saponified, with the production of isocoumarins (B. 25, 3566; 27, 827):

$$C_{e}H_{4} \underbrace{\stackrel{CH_{3}(CN)}{CN} \stackrel{(RCO)_{2}O}{\longrightarrow}}_{C_{e}H_{4}} \underbrace{\stackrel{C(CN)}{\frown}_{CO} \stackrel{CR}{\longrightarrow}}_{OOCR} \xrightarrow{H_{2}O} C_{e}H_{4} \underbrace{\stackrel{CH}{\frown}_{CO} \stackrel{CR}{\longrightarrow}}_{CO} C_{O}$$

Benzo- and dibenzo- γ -pyrones are derived from γ -pyrone. Various yellow vegetable dyes are to be included in this group (v. Kostanecki).

Chrysin, fisetin, and quercetin are obtained from β-phenylbenzo-γ-pyrone, so-called favone (flavus, "yellow"). Judging from their decomposition products, the following formulas may probably be ascribed to them:

$$(BO)_{4[3,5]}C_{6}H_{6} \begin{cases} [1]O-CC_{6}H_{6} \\ [1]O-CC_{6}H_{2}(OH)_{8} \\ [1]O-CC_{6}H_{2}(OH)_{8} \\ [2]O-C(OH) \end{cases} \\ Charyoin \qquad (HO)_{4[3,5]}C_{6}H_{2} \begin{cases} [1]O-CC_{6}H_{2}(OH)_{8} \\ [2]O-C(OH) \\ [2]O-C(OH) \\ [2]O-C(OH) \end{cases}$$

Chrysin, C₁₆H₁₆O₄, melting at 275°, occurring in the blossoms of different papers, may be decomposed into phloroglacia, beasoic acid, and acetic acid.

Finetin, C₁₆H₁₆O₄, from Rhus cations, and Quebrache Colorade (B. 29, R. \$53), on be resolved into resorcinol, protocatechnic acid, and glycollic acid, while Querostia, C₁₆H₁₆H₁₇, melting at 250°, and obtained from the glucoside querciaria, found in the but of Queross tinctoria, as well as from the buds of the horse-chestant, and from cuious (B. 29, R. 779), may be broken down into phloroglacia, protocatechnic acid, and glycollic acid (B. 38, 2302).

Murcicatin C. H. O. a vallow due research in the back of Affinion ment is probable.

Myricetin, C₁₆H₁₆O₂, a yellow dye present in the bank of Myrice mags, is probably presenting with the formula (OH) [2 5]C H [1]O—CC₆H₂(OH)₀ (R as R. exyquercetin, with the formula (OH),[3,5]CaH [2]CO—C(OH)

778). Compare B. 30, 1077, for the synthesis of flavone and its derivatives.

The Kanthones (ξωθός, yellow) or diphenylene ketone exides are dibenzopyrones. They can also be viewed as keto-derivatives of Xanthene, or methylenediphenylene axide (B. 26, 72):

The xanthones possess a chromogenic nature. They are allied to thioxanthones (p. 526), the acridones (p. 560), and thiodiphenylamines. Generally they are formed by condensing salicylic acid with phenols through the agency of sulphuric acid, acetic anhydride, etc. (B. 21, 502):

$$(HO) C_6 H_8 < H \\ CO \\ OH \\ + CO \\ OH \\ C_6 H_4 \\ \hline \longrightarrow (HO) C_6 H_8 < CO \\ O > C_6 H_4 \\ \hline \longrightarrow (HO) C_6 H_8 < CO \\ O > C_6 H_4 \\ \hline \longrightarrow (HO) C_6 H_8 < CO \\ O > C_6 H_4 \\ \hline \longrightarrow (HO) C_6 H_8 < CO \\ O > C_6 H_8$$

Xanthene, Methylene Diphenylene Oxide, C12H100, melting at 99° and boiling at 312°, is produced by the reduction of xanthone and oxyxanthones. o-Dioxybenzophenone is formed when it is fused with caustic potash (p. 348). Tetramethyldiamidoxanthene, Tetramethyldiamidodiphenyl methane oxide,

 $(CH_1)_2NC_6H_3<\frac{CH_2}{O}>C_6H_2N(CH_2)_2$, melting at 116°, obtained by the action of sulphuric acid upon tetramethyldiamidodioxydiphenylmethane, the leuco-base of the dye pyronine (see below) (B. 27, 3303). Dinaphthoxanthene, $C_{19}H_6 < {CH_5 \over O} > C_{19}H_6$, melting at 199°, results upon condensing formic aldehyde with β -naphthol (p. 410) (B. 26, 84). Xanthydrol, $C_8H_4 < \frac{CH(OH)}{O} > C_8H_4$, is formed in the careful reduction of xanthone.

It is a substance which changes quite readily. Like benzhydrol (p. 344), it shows a great tendency to split off water and pass into its ether—zanthydrol ether, (C₁₂H₆O)₂O, melting at 200° (B. 26, 1276; compare also B. 28, 2310).

Xanthone, Diphenylene Ketone Oxide, C₁₂H₈O₂, melting at 174° and boiling at 250°, is produced from salicylic phenyl ether or phenylsalicylic acid by the action of concentrated sulphuric acid from o-diamidobenzophenone with nitros acid (B. 27, 3363); and when fluorane and hydrofluoranic acid (p. 365) are distilled with lime (B. 25, 2119). It does not unite with hydroxylamine or phenylhydrazine. It forms dioxy-benaophenone on careful fusion with KOH.

Just as benzophenone yields tetraphenylethylene, so xanthone is converted by zincdust, bydrochloric acid, and acetic acid into tetraphenylene-ethylene dioxide, O[CaHa]s-C: C[C₂H₄]₂O, melting at 315° (B. 28, 2311).

Oxyxanthones, $C_{13}H_7(OH)O_2$: The four possible isomerides have been prepare condensing salicylic acid with resorcinol, hydroquinone, and pyrocatechol (B. 1652; 26, 71).

Euxanthone, 1,7-Dioxyxanthone, $HOC_6H_3 < {}^{CO}_O > C_6H_3OH$, consists of ye needles melting at 237° and subliming. It occurrence and in combination with curonic acid (1, 585) as euxanthinic acid in Indian yellow. It has been synthetic produced by the action of acetic anhydride upon two molecules of β -resorcylic acid hydroquinone carboxylic acid (B. 24, 3982; 27, 1989; A. 254, 265).

produced by the action of acetic anhydride upon two molecules of β-resorcylic acid hydroquinone carboxylic acid (B. 24, 3982; 27, 1989; A. 254, 265).

3,6-Dioxyxanthone results on heating 0,,p₂-tetraoxybenzophenone, a decompos product of fluorescein chloride in the alkali fusion. It consists of colorless needles. alkaline solutions show a deep violet-blue fluorescence (B. 30, 969). 1,3,7-Tric xanthone, Gentisein, C₁₈H₇(OH)₂O₂(+2H₂O), melting at 315°, is obtained syntically from hydroquinone carboxylic acid and phloroglucin. It dyes mordanted cott bright yellow. Gentisin (B. 27, 190; 29, R. 221), occurring in the root of Gent. Intera., is its monomethyl ether. Compare B. 25, 1641, for the dinaphthoxanthor phenonaphthoxanthones, etc.

The fluoranes, fluorones, and fluorimes are related to the xanthones (B. 25, 2: 27, 2887):

These are the parent-substances of the fluorescein dyes (pp. 363, 366). Pyron (CH₃)₂N. C₆H₅C(H₅N(CH₃)₂Cl, belongs to the fluorimes. It is produce the exit of water from and the oxidation of dioxytetramethyldiamidodiphenylmeth The leuco-compound of pyronine is 2,7-Tetramethyldiamidoxanthene, meltin 116°. Pyronine may be oxidized in alkaline solution to tetramethyldiamidoxanthemelting at 241°. Pyronine colors silk and imparts a beautiful rose-color to cotton (B 2896, 3304; 29, R. 1129).

2. SIX-MEMBERED RINGS CONTAINING ONE S-MEMBER.

Six-membered rings containing sulphur as the hetero-atom are pres

in the derivatives of hypothetical penthiophene,
$$(a_i)^{CH}$$
 CII $(a_i)^{CH}$ CII

a ring-homologue of thiophene. They are, however, not very numero

β-Methyl Penthiophene, C₅II₅(CH₃)S, is an oil boiling at 134° with sp. gr. o (19°). It is produced from a-methyl glutaric acid by the action of P₂S₃, similar to formation of thiophene from succinic acid (p. 453) (B. 19, 3266):

cH₂
$$<$$
CH₂ $<$ CH₂ $<$ CH₃ $=$ CO₂H $=$ P₂S₃ $=$ CH₂ $<$ C(CH₃) $=$ CH $=$ CH $=$ Se-Methyl Glutaric Acid

It is colored the same as the thiophenes by isatin or penanthraquinone and sulpl acid. It is more unstable than the thiophenes and is destroyed completely by very d potassium permanganate. Acetyl chloride and Al₂Cl₆ convert it into acetyl to penthiophene, C₂H₆(COCH₂)(CH₂)S, boiling at 250°.

A dibenzoderivative of penthiophene is found in Thioxanthene or methylene is found in Thioxanthene is fou

Thioxanthone, benzophenone sulphide, $C_{13}H_6OS = C_6H_4 < {}^{CO}_S > C_6H_6$, melting at 207° and boiling at 340°, is the ketone of the preceding body. Being an analogue of xanthone, it is formed similarly to the latter from thiophenylsalicylic acid and sulphinic acid (A. 263, I). It forms a sulphone, $C_6H_4 < {}^{CO}_S > C_6H_4$, on oxidation.

3. SIX-MEMBERED RINGS CONTAINING AN N-MEMBER

I. PYRIDINE GROUP.

Pyridine, C₂H₃N, is the parent substance of many vegetable alkaloids. Its compounds, like those of benzene, show great stability toward oxidizing agents, inasmuch as those having side-chains—e. g., the alkyl pyridines, C₅H₄(CH₃)N, C₅H₃(CH₃)₄N, etc.—are converted on oxidation, like the alkyl benzenes, into acids, the pyridine nucleus not being attacked. As in the case of the aromatic derivatives, this behavior is assumed to be due to the existence of a six-membered ring, consisting of five carbon atoms and one nitrogen atom, similar to the six-membered benzene ring. Pyridine is the hydrogen derivative of this ring: it is benzene in which one CH- or methine group is replaced by a nitrogen atom.

The following structural formulas have been proposed for pyridine: (1) the formula of Körner; (2) the formula of Riedel. They differ in that in Körner's formula the nitrogen atom is linked to two carbon atoms, while in that of Riedel it is combined with three carbon atoms. To this formula that (3) of Bamberger and v. Pechmann adds itself. It is a centric formula (B. 24, 3151), for which there are no experimental proofs (see p. 40):

To determine whether pyridine contained an N-atom in union with two or three carbon atoms, Kekulé* arranged a series of experiments based on the following considerations. Assuming that in the pyridine formulas I and II the a-hydrogen atoms are replaced by two hydroxyl groups, the connection between the nitrogen and the carlon atom now carrying oxygen will be less intimate. This becomes evident if we imagine that the C(OII)-groups have rearranged themselves into the keto-form:

* B. 23, 1265, and private communications.

The ordinary mode of writing pyridine obscures the connection of these pyridine derivatives with the aliphatic bodies, the derivatives of which they may be considered. This relation is more evident from the following representations:

It becomes at once plain that formula I, represents a glutaconic acid derivative—the imide of glutaconic acid; while formula II, is a β -amidoglutaconic acid derivative—an inner imide of β -amidoglutaric acid. According to formula II, the inner imide of β -amidoglutaric acid would have a constitution similar to that suggested by Kekulé for furarimide, and as the latter is supposed to be prepared from ammonium malate, Kekulé began with β -oxyglutaric acid (1, 494), and attempted by heating its ammonium salt to prepare homofumarimide, but without result. Again, he sought to pass from β -oxyglutaric acid diamide (+2H₂O), from glutaconamic acid and glutacondiamide, to pyridine. In fact, these three substances, when acted upon with concentrated sulphuric acid, yield glutaconimide or dioxypyridine (1, 467) of formula I.

The presence of the imido-group was proved by converting the sodium compound of

The presence of the imido group was proved by converting the sodium compound of glutaconimide into methyl glutaconimide, from which hydriodic acid liberates methylamine, and by the preparation of nitrosoglutaconimide. The decomposition of glutaconimide gave glutaconic acid. The objection that here β -amido-glutaric acid was first produced in conformity with formula II,, and that from this glutaconic acid arose through the elimination of ammonia, is contradicted by the deportment of the β -amidoglutaric acid, which, under like conditions, does not yield glutaconic acid. The β -amidoglutaric acid, too, yielded no glutaconimide, or any amount of an isomeric body; the ring-forma-

tion failed.

The connection of glutaconimide with pyridine, which results from the distillation of the former with zinc-dust, Kekulé demonstrated by converting glutaconimide with PCl_b into pentachlorpyridine, identical with an analogous body obtained from pyridine.

With these facts as bases, Kekulé held it as highly improbable that the nitrogen of

With these facts as bases, Kekulé held it as highly improbable that the nitrogen of pyridine was joined to the three carbon atoms a, a_1 , γ , as required by Riedel's formula, whereas the Körner formula is in complete harmony with the experimental results, and is supported by them.

supported by them.

The centric formula of pyridine, in which the "central linkages" are in unstable equilibrium, permits of many transitions and changes without displacement of the double linkage, and therefore isolates pyridine from compounds like glutaconic acid and gluta-

conimide, which bear close genetic relations to pyridine.

The production of pyridine from piperidine (hexahydropyridine or pentamethylene imine, p. 539) is important in determining its constitution. It results upon heating HCl-pentamethylene diamine or δ-chloramylamine (1, 311):

$$CH_3$$
 CH_3
 CH_3
 CH_4
 CH_5
 CH_5
 CH_5
 CH_6
 CH_7
 CH_7

The same may be said of quinoline and isoquinoline (pp. 541, 554), which are benzopyridines which have been obtained synthetically:

$$CH = CH - C - CH = CH$$

$$CH = CH - C - CH = CH$$

$$COOH \cdot C - CH = CH$$

$$COOH \cdot C - CH = CH$$

$$CH - CH - CH = CH$$

$$COOH \cdot C - CH = CH$$

$$CH - CH - CH = CH$$

$$CH - CH$$

$$CH$$

Pyridine and a series of its homologues are produced in the dry dis lation of nitrogenous carbon compounds, hence they are present in o tar, in the tar from shales, in that from peat (very little), and in bone (compare p. 48). Compare B. 30, 224, for the occurrence of pyridin in fusel oil.

Anderson (1846) isolated the first pyridine bases from bone-oil. These were exhaustively investigated in 1879 and in the years following by Weidel and his stail

also by Ladenburg and others.

also by Ladenburg and others.

Their presence in bone-oil is due to the reciprocating action of fats (glycerol ental) and substances containing ammonia (albumin, etc.); the acrolein arising from the fat probably condensing with the ammonia to pyridines (see synthetic method I). Bure glue, free from fats, does not yield pyridine bases, but mainly pyrrols (p. 456) (B. IS. 83). At present the pyridine bases are obtained chiefly from coal-tar (A. 267, I). They are found in the acid used for the purifying of the tar. They can easily be included that it in the form of the "pyridine-base mixture," which at present is employed in Games for the "denaturation" of spirit.

Synthetic Methods for the Production of Pyridine Derivatives:

1. Alkyl pyridines are formed on heating aldehyde ammenias alone or with aldehydes and ketones (A. 59, 298; 155, 310; B. 23, 685, etc.):

$$CH_3$$
. CHO . $NH_3 + 3CH_3$. $CHO = C_3H_3(CH_3)(C_2H_5)N_2 + 4H_4O$

- Methyl-8-ethyl Pyridine (Aldehyde Collidine).

In this reaction evidently several aldehyde molecules condense to unsaturated aldehydes, with long carbon chains, which in turn condense with ammonia, forming riags β-Picoline (p. 532) can also be made by heating glycerol with P₂O₅ and ammoniscal substances—e.g., acetamide, or, better, ammonium phosphate (B. 24, 1676), when pyrazines are produced as by-products (see these).

2. A method frequently pursued in synthesizing pyridine derivatives consists in the condensation of \(\beta\text{-diketo-compounds}\) with aldehydes and

ammonia (pyridine syntheses of Hantzsch):

Example a.—Acetoacetic ester (2 mols.), acetaldehyde, and ammonia (or aldehyde ammonia) yield dihydrocollidine dicarboxylic ester or 1,3,5trimethyldihydropyridine dicarboxylic ester, which, by the withdrawal of two hydrogen atoms, may be easily converted into its corresponding pyridine derivative (A. 215, 1; B. 18, 2579):

The acetaldehyde can be replaced by its homologues, by formic aldehyde or benzaldehyde (B. 29, R. 842), and the second molecule of acetoacetic ester by the 1,3-diketones-e.g., acetyl acetone, benzoyl acetone, etc. (B. 24, 1669). In the preceding reaction it may be assumed that the aldehyde and acetoacetic ester first combine to ethylidene diacetoacetic ester, CH₃. CH[CH(CO₃R). COCH₃]₃. This is a 1,5-diketone derivative, which unites with ammonia to a pyridine ring, just as 1,4-diketones and ammonia form pyrrols (p. 456). Consequently, dihydrocollidine dicarboxylic ester is produced in excellent yield in the condensation of ethylidene acceptance ester and f-ammonia form pyrrols (p. 456). crotonic acid ester, in that the latter attaches itself to the unsaturated linkage of the former, with consequent ring formation (B. 24, 1667).

Furthermore, pyridine derivatives are easily obtained by condensing oxymethylene parametric esters with β -amidocrotonic esters (B. 26, 2734), or, in general, if NH₃ be

bred to act upon 1,5-diketones of the constitution, CH—CO—, which are pre-

used by condensing ethoxymethylene acetoacetic ester and analogously constituted compounds with β -ketonic esters or 1,3-diketones (B. 28, R. 491):

Compare B. 28, R. 1002, for another explanation of the mechanism of this reaction.

**Brample b.—1,3-Dimethylpyridine-2-carboxylic ester forms upon digesting aceto
**Ester (1 mol.) with acetaldehyde (2 mols.) and ammonia:

$$\begin{array}{cccc} CH_3 & CH_3 \\ CH_6 & OCH & CH_2 \cdot CO_2R & \longrightarrow & CH = \overset{\uparrow}{C} - C \cdot CO_2R \\ HCO & NH_1 & CO \cdot CH_3 & CH = N - \overset{\downarrow}{C} \cdot CH_3 & (+ 3H_2O + 2H). \end{array}$$

The mechanism of this reaction is probably similar to that in example a. The dihydro-product formed at first is probably oxidized by the excessive aldehyde to the corresponding pyridine. This reaction can also be varied by the use of different aldehydes.

sponding pyridine. This reaction can also be varied by the use of different aldehydes.

3. 1,5-Diketones, the keto-groups of which are combined with phenyl residues (1,3-dibenzoyl paraffins), yield pyridines when acted upon with hydroxylamine (A. 281, 36):

$$\textbf{C}_{\textbf{g}}\textbf{H}_{\textbf{g}}\textbf{C}\textbf{H} \underbrace{ \begin{matrix} \textbf{C}\textbf{H}(\textbf{C}_{\textbf{g}}\textbf{H}_{\textbf{b}}) - \textbf{CO}.\textbf{C}_{\textbf{g}}\textbf{H}_{\textbf{b}} \\ \textbf{C}\textbf{H}(\textbf{C}_{\textbf{g}}\textbf{H}_{\textbf{b}}) - \textbf{CO}.\textbf{C}_{\textbf{g}}\textbf{H}_{\textbf{b}} \end{matrix}}_{\textbf{C}\textbf{H}_{\textbf{c}}\textbf{O}} + \textbf{N}\textbf{H}_{\textbf{2}}\textbf{O}\textbf{H} = \textbf{C}_{\textbf{g}}\textbf{H}_{\textbf{b}}\textbf{C} \underbrace{ \begin{matrix} \textbf{C}(\textbf{C}_{\textbf{g}}\textbf{H}_{\textbf{b}}) = \textbf{C}\textbf{C}_{\textbf{g}}\textbf{H}_{\textbf{b}} \\ \textbf{C}(\textbf{C}_{\textbf{g}}\textbf{H}_{\textbf{b}}) - \textbf{C}\textbf{C}\textbf{C}_{\textbf{g}}\textbf{H}_{\textbf{b}} \end{matrix}}_{\textbf{N}} + 3\textbf{H}_{\textbf{2}}\textbf{O}$$

Pyridines are also produced by the dry distillation of certain oximes of diolefine monoketones (B. 28, 1726; 29, 613):

$$\begin{array}{c|c} CH \longrightarrow CH = CH & CH \longrightarrow CH \longrightarrow CH \longrightarrow CH \\ C_aH_aCH & HON = C. CH_a & CH \longrightarrow C_aH_aC \longrightarrow N \longrightarrow CCH_a \\ Cinnamenylidene Acetoxime & a,a_1-Phenylmethyl Pyridine. \end{array}$$

4. Pyridines are produced by oxidizing the synthetic hexahydropyridines, piperidines, or pentamethyleneimides (p. 538) with sulphuric acid or silver acetate (B. 25, 1621):

$$\begin{array}{c} \textbf{CH_1-CH_2-CH_2Br} \\ \textbf{CH_3-CH_3-NH_2} \\ \textbf{4-Bromamylamine} \end{array} \xrightarrow{-\textbf{HBr}} \begin{array}{c} \textbf{CH_1-CH_3-CH_3} \\ \textbf{CH_3-CH_3-NH} \\ \textbf{Piperidine} \end{array} \xrightarrow{-\textbf{6H}} \begin{array}{c} \textbf{CH=CH-CH} \\ \textbf{CH=CH-N} \\ \textbf{Pyridine.} \end{array}$$

5. Oxypyridine derivatives (pyridones) result from the action of ammonia upon the pyrone compounds; the linking oxygen atom of the pyrones is replaced by the NH-group.

6. e,e₁-Dioxypyridines, which can also be regarded as imides of glutaconic acid and its homologues, are obtained from glutaconamic acid, etc., by a ring-formation (comp. 1, 467; 11, 527); similarly, citrazinic acid, dioxypyridine carboxylic acid, is prepared by the action of ammonia upon aconitic ester; also from citramide (1, 530).

7. Further, glutaconimide derivatives may be made synthetically by condensing acetoacetic esters and cyanacetic ester with ammonia or primary amines (B. 29, R. 654; C. 1897, 1, 927):

Similarly, a-pyridones are obtained by condensing β -amidoketones—e. g., diacetonamine, CH₂. CO. CH₂. C(CH₃), NH₂, or acetyl acetonamine, CH₃. CO. CH: C(CH₄). NH₄, with cyanacetic ester (B. 26, R. 943).

8. The fact that β -chlor- and β -brom-pyridine can by produced by heating potassium.

pyrrol with CHCl₃ and CHBr₃ is of interest. Pyrrol and sodium ethylate may be used as a substitute for potassium pyrrol. Pyridine results if CH₂I₃ be used, and with benzal chloride the product is β -phenylpyridine (B. 20, 191). Alkylpyridines (B. 19, 2196) are similarly formed from alkylpyrrols upon heating them with concentrated hydrochloric acid. Compare the conversion of alkyl indols into quinoline derivatives (p. 544).

Behavior: The pyridine bases are colorless liquids with a peculiar Pyridine is miscible with water. The solubility of the higher members grows rapidly less. Frequently they are more soluble in cold than in hot water. The pyridines are tertiary bases and form crystalline salts with one equivalent of the acids.

- 1. Salts.—The platinum double salts of the formula (C₅H₅N. HCl)₅-PtCl, lose two molecules of hydrochloric acid upon prolonged boiling and form (C₆H₆N)₂PtCl₄ (see pyrazoles, p. 482). The pyridines form addition compounds with many inorganic salts. These, with HgCl₂ and AuCl₃, are characteristic and serve for the separation of the individual bases (A. 247, 1; comp. C. 1897, II, 129, 311).
 - 2. Alkyl iodides and pyridines form alkyl pyridinium iodides.

The corresponding alkyl pyridinium hydroxides appear to be very unstable. If they be treated with sodium hydroxide and potassium ferricyanide an atomic rearrangement ensues and n-alkylpyridones result:

$$HC \stackrel{CH-CH}{\swarrow} N \stackrel{OH}{\swarrow} \longrightarrow CH \stackrel{CH-CO}{\swarrow} NCH_{8}$$

(B. 25, 3326; compare also the quinolinium compounds, p. 545).

- 3. The pyridines also unite with chloracetic acid and its homologues, with formation of pyridine betaines.
- 4. When the alkyl pyridinium iodides are heated to 300° alkyl pyridines result, with a migration of the alkyl-group to a- or \(\gamma\)-C-atom (Ladenburg, B. 17, 772). This is analogous to the production of homologous anilines from n-alkyl anilines (p. 72).
- 5 (a). a-Methyl pyridines condense with aldehydes on heating with water; this is in the nature of the aldol formation. The alkines, secondary alcohols, result (B. 23, 2709). Thus, a-picoline and acetaldehyde form a-picolyl methyl alkine, (CH₄N)CH₂.-CHOH.CH₃. The compounds with chloral are especially characteristic (B. 26, 1414).
- 5 (b). Pyridines with unsaturated side-chains are formed on heating a-methyl picolines with aldehydes and zinc chloride. Thus, a-picoline and benzaldehyde yield stilbazole, (C5H4N)CH: CHC6H5 (p. 533).
- 6. Oxidizing agents—e. g., nitric acid, chromic acid—as a rule do not attack the pyridines. All the homologous pyridines, on the other

PYRIDINE. 531

hand, and even the phenyl pyridines are oxidized by potassium permanganate to *pyridine carboxylic acids*, which finally yield pyridine upon distillation with lime.

7. Reducing agents (sodium and alcohol) convert the pyridine bases into hexahydropyridines, or piperidines, which can be decomposed by various methods into fatty bodies (compare piperidine decompositions, p. 539). The pyridines are reduced to paraffins when heated with hydriodic acid. Pyridine yields pentane.

8. Halogen, nitro-, and sulpho-derivatives are prepared with far more

difficulty from the pyridines than from the benzenes.

Isomerides.

The derivatives produced by the replacement of the hydrogen atoms in pyridine can essily be deduced in their possible isomerisms from the given structural formulas, and are perfectly analogous to the isomerisms of the benzene derivatives. Representing the five hydrogen atoms, or the affinities of the pyridine nucleus, with numbers or letters, corresponding to the diagram—

$$\begin{array}{c|c}
3 & CH & CH \\
CH & CH & CH \\
4 & 5
\end{array}$$
 or $\gamma \left(\begin{array}{c} \beta_1 & a_1 \\
\beta_1 & a_2 \\
\end{array}\right) N$,

then the positions, 1 and 5, also 2 and 4 (as in benzene), are similar (p. 33). The first may be designated the ortho-, the latter, the meta-positions—while the position 3, occurring only once, corresponds to the pura of benzene. From this we conclude that the mono-derivatives of pyridine, $C_5H_4(X)N$, can exist in three series, while six isomerides are possible with the di-derivatives $C_5H_3(X_5)N$. This is verified by the existence of three methyl, three propyl- and phenyl-pyridines, $C_5H_4(R)N$, of three pyridine-mono-carboxylic acids, $C_5H_4(CO_2H)N$, of six dicarboxylic acids, etc. The determination of place for the pyridine derivatives usually follows from their conversion into carboxylic acids of pyridine.

Constitution of the Pyridine Monocarboxylic Acids.—The constitution of pyridine-a-carboxylic acid or picolinic acid and pyridine- β -carboxylic acid or nicotinic acid is evident from its production in the oxidation of a- and β -phenylpyridines. These latter bodies have been obtained from a- and β -naphthoquinoline. When these are oxidized the first products are a- and β -phenylpyridine dicarboxylic acids, which upon the loss of \mathbf{zCO}_3 become phenylpyridines. This proof of constitution presupposes, therefore, the constitution of a- and β -naphthoquinolines. The diagram represents the derivation of the constitution of picolinic acid:

-Naphtho-quinoline

e-Phenylpyridine Dicarboxylic Acid

a-Phenyl Pyridine

Pyridine-a-carboxylic Acid, a-Picolinic Acid.

The behavior of the pyridine dicarboxylic acids leads to a simpler deduction of the position of their atoms (B. 18, 2967). Quinolinic acid (pyridine dicarboxylic acid), formed by the oxidation of quinoline, has the position (1,2), and cinchomeronic acid, from isoquinoline, has the position (2,3). Quinolinic acid loses one molecule of carbon dioxide when heated and forms nicotinic acid, while cinchomeronic acid yields nicotinic acid and isonicotinic acid; therefore nicotinic acid is $\beta = 2$ and isonicotinic acid $\gamma = 3$.

Pyridine, C_kH_kN , boiling at 114.8°, with sp. gr. 1.003 (0°), can be prepared from bone-oil, and is obtained from all the pyridine-carboxylic acids on distillation with lime. Its hydrochloride, C_kH_kN . HCl, is

deliquescent, and with platinum chloride it forms a double salt, (C,H,-N. HCl), PtCl4, melting at 240°. See B. 29, R. 295, for pyridine mercury compounds. Its iodmethylate melts at 117° (B. 29, R. 994). Pyridine betaine, C₅H₅N CH₂CO, melting with decomposition at 150°, is formed by the interaction of pyridine and chloracetic acid (B. 23, 2609). Compare 1, 521; B. 26, R. 54, for the action of pyridine upon acetyl chloride and benzoyl chloride. Sodium and alcohol reduce it to piperidine, while normal pentane is produced when it is heated with hydriodic acid.

1. Homologous Pyridines. Methyl Pyridines, C₈H₄(CH₃)N, Picolines (from

pix, tar; because they were obtained from coal-tar):

a-Picoline boils at 130°; its sp. gr. is 0.965 at 0°, and it is oxidized by potassium permanganate to picolinic acid. β -Picoline boils at 143°; its sp. gr. is 0.977. It is formed when strychnine is distilled (B. 23, 3555), and upon heating glycerol with P₂O₃ and ammonium phosphate; also by heating trimethylenediamine hydrochloride (B. 23, 2730). It yields nicotinic acid on oxidation. y-Picoline boils at 144°. Its sp. gr. is 0.974 at 0°. It has also been prepared by heating pyridine iodmethylate (p. 531). It yields isonicotinic acid when it is oxidized.

Dimethyl Pyridines, Lutidines, C₅(CH₂)₂H₂N. Bone-oil contains mainly: aa₁-Lutidine, boiling at 142°, with sp. gr. 0.942; a_{ij} . Lutidine, boiling at 157°, with sp. gr. 0.9493; and β_{ij} . Lutidine, boiling at 164° (B. 21, 1006; 29, 2996). β_{ij} . Lutidine, from the corresponding carboxylic acid, boils at 170° (B. 23, 1113).

a-Ethyl Pyridine, $C_5H_4(C_2H_5)N$, boils at 148°; its sp. gr. is 0.949 at 0°. γ -Ethyl Pyridine boils at 165°; its sp. gr. is 0.952 at 0°. These two compounds result upon heating pyridine ethyl iodide. β -Ethyl Pyridine has been obtained, together with the

3-body, from cinchonine and brucine on heating with caustic potash. It boils at 166°. Sym. (1,3,5) Trimethyl Pyridine, C₆H₄(CH₂)₂N, collidine, is obtained from synthetic dihydrocollidine dicarboxylic ester (p. 528) by oxidation, saponification, and the elimination of carbon dioxide. It boils at 172°. 1,3,4-Collidine, boiling at 165-168°,

occurs in coal-tar (B. 29, 2998).

(1,4) Methyl-Ethyl Pyridine, C₅H₅(CH₅)(C₂H₅)N, has been prepared from various aldehyde compounds, hence called aldehydine or aldehydcollidine. It boils at 178°.

a Propyl Pyridine, Conyrine, C₅(C₃H₇)H₄N, is produced on heating conine with

zinc-dust. It boils at 167°.

a Isopropyl Pyridine is produced, together with the γ-compound, when pyridine propyl iodide or isopropyl iodide is heated. It boils at 158°.

Parvuline, v-Tetramethyl Pyridine, boiling at 227-230°, occurs in coal-tar (Β.

β₁β₁·Dibenzyl Pyridine, C₅H₃(C₁H₇)₂N, boiling at 89°, is formed in the condensation of benzaldehyde with benzoyl piperidine (p. 540) (A. 280, 36).

a- and β Phenyl Pyridine, C₅(C₆H₅) H₄N, boiling at 269° and 270°, result from the elimination of 2CO₂ from their carboxylic acids, the decomposition products of a- and β -naphthoquinoline. The a-body can also be made by heating the corresponding a-pyridone with zinc-dust (B. 29, 1678).

p Nitrophenyl Pyridine, melting at 117°, is obtained from nitrosodiazobenzene and pyridine. By reduction it yields p-amidophenylpyridine, melting at 102°, which yields a-phenyl pyridine (B. 29, 167). Dinitrophenyl Pyridine melts at 118° (B. 29, 279). y-Phenyl Pyridine, melting at 77° and boiling at 274°, results from a transposition of the condensation product of acetoacetic ester with benzaldehyde and ammonia

(p. 528).

 a, a_1 -Phenyl Methyl Pyridine, $C_5(C_6H_5)(CH_3)H_3N$, boiling at 281°, is obtained from cinnamylidene acetoxime (p. 529 and B. 28, 1727). a, a_1 -Diphenyl Pyridine, melting at 82°, has been obtained (1) by distilling the oxime of cinnamylene-acetophenone (method 3, p. 529); (2) from a, a_1 -diphenyl-y-pyridine-carboxylic acid, produced on heating diphenacyl-malonic acid with ammonia; and (3) by oxidizing a-phenylnaphthocinchoninic acid (B. 29, 798; 30, 1499) Tetra- and Pentaphenyl Pyridines, melting at 179° and 240°, are produced from desoxybenzoin benzylidene acetophenone,

and from benzamarone and N11,OH (p. 529) (A. 281, 50; B. 26, 440). γ - γ -Dipyridyl, (C₈H₄N)₂ + 2H₄O, melting at 73° (114°) and boiling at 305°, is produced, together with an oily, polymeric pyridine (C₈H₅N)x, when sodium acts upon pyridine (B. 24, 1478). $\beta_1\beta_1$ -Dipyridyl, melting at 68° and boiling at 287°, is obtained from its dicarboxylic acid, an oxidation product of phenanthroline (p. 554). Compare B. 21, 1077, for another dipyridyl.

Vinyl Pyridine, C,H,(C,H,)N, results when pyridine vapors are conducted, together with ethylene, through a tube heated to redness, as well as from a picolyl alkine

by the loss of water, and from pyridyl-β-brompropionic acid (p. 538) by the exit of CO₃ and HBr. It boils at 160° (B. 20, 1644; A. 265, 229).

a-Allyl Pyridine, C₅H₄(C₃H₅)N, is produced when picoline and paraldehyde are heated to 200° (A. 247, 26). It boils at 290°. Sodium and alcohol convert it into propyl piperidine (inactive conine, p. 562).

Styryl Pyridine, Stilbazole, Cg(CH: CHCgHg)HgN, melting at 61° and boiling at

325°, is formed from a-picoline with benzaldehyde and zinc chloride.

2. Halogen Pyridines: The pyridines containing halogens in the nucleus are obtained with difficulty by the direct action of the halogens upon the pyridines. Bromine particularly replaces the alkyl group in the homologous pyridines very easily (B. 25, 2985; 28, 1759). The replacement of the pyridine hydrogen atoms is more easily effected upon heating pyridine or the oxypyridines with phosphorus or antimony pentachlorides.

a-Chlor-pyridine, melting at 166°, results on treating a-oxypyridine with PCl₃. β -Chlor-pyridine, boiling at 148°, and β -Brom-pyridine, boiling at 170°, are formed when CCl₂H or CBr₃H acts upon pyrrol-potassium (p. 530). a-Phenyl-a-chlor-pyridine, melting at 34°, is obtained from phenylpyridone (B. 29, 1679). Dichlor-pyridine, melting at 67°, and trichlor-pyridine, melting at 50°, result from the action of PCI₈ upon barium pyridine disulphonate. a, γ -Dichlor-picoline, boiling at 206°, is obtained from dioxypicoline (B. 28, R. 644). Tetrachlor-pyridine, melting at 80-85°, and Pentachlor-pyridine, C_6Cl_6N , melting at 124-125°, are prepared from pyridine and phosphorus pentachloride. The same reagent converts dioxypyridine (glutaconimide) into perchlorpyridine (Kekulé, p. 527).

3. Pyridine Sulphonic Acids are formed, together with pyridine, on heating piperi-

dine with concentrated sulphuric acid.

\(\beta\cdot\)-Pyridine Sulphonic Acid, C_kH₄(SO₃II)N, also results on treating pyridine with sulphuric acid. β -Cyan-pyridine, melting at 49°, is formed when its sodium salt is distilled with potassium cyanide. It is the nitrile of nicotinic acid (p. 536) and yields β -oxypyridine on fusion with caustic potash.

4. Nitro-pyridines: Nitration of the pyridine nucleus seems only possible when NH₂-, OH-, or similar groups are present, which, as in the case of benzene, facilitate the

nitration (p. 149).

The nitration of β -oxypyridine (p. 534) in the form of its acetyl ester with nitric acid containing N₂O₃ gives rise to two nitro-oxypyridines, melting at 211° and at 295-298° with decomposition; also a dinitro-oxypyridine, melting at 133° (B. 28, R. 911). See nicotinic acid (p. 536) for the nitroamidonicotinic acids.

5. Amido-pyridines have been obtained from the pyridine acid-amides with bromine and caustic potash (Hofmann's reaction), and also by the exit of CO, from amidopyridine

carboxylic acids.

a-Amido-pyridine, melting at 56° and boiling at 204°, is obtained from the amide of a-picolinic acid; also from a- and a_1 -amido-nicotinic acid (B. 27, 1317, R. 410; A. 288, 253). β -Amido-pyridine, melting at 64° and boiling at 251°, is formed in the action of bromine and caustic potash upon the amide of nicotinic acid (B. 28, R. 322). y-Amido-a,a₁-lutidine, C₅H₂(CH₃)₂(NH₂)N, melting at 186° and boiling at 246°, is obtained from amido-lutidine dicarboxylic acid (B. 27, 1325). Chlorinated a-amidopyridines have been obtained by the action of PCl₅ upon β -oxyglutaramide. a-amido-pyridine, C. HCl₂(NII₂)N, melts at 143-144°.

6. Oxypyridines: They correspond to the amidophenols, as they form salts both

6. Oxypyridines: They correspond to the amidophenols, as they form salts both with bases and acids. They are formed with special ease from the oxypyridine carboxylic

acids by the elimination of the carboxyl groups. The most of these acids have been produced by the action of ammonia upon the corresponding pyrone derivatives. Ferric chloride imparts a red color to nearly all their solutions. On the other hand, the a- and y-oxypyridines manifest the deportment of cyclic imides or lactams. They must be viewed as keto or oxo-compounds of the hydropyridines, and are called, therefore, pyridones. The following formulas have been considered for the a- and y-monoxypyridines:

I.
$$CH = CH - C(OH)$$
 N

 $CH = CH$ OH

 $CH = CH$ OH

 $CH = CH$ N

 $CH = CH$ OH

 $CH = CH$ NH

 $CH = CH$ NH

Although it is undetermined which of the two possible representations belongs to the free oxy-bodies, alkyl derivatives are obtained from both in which the alkyl residue replaces the imide or hydroxyl hydrogen (B. 24, 3144) (1, 363). The following formulas should also be considered for the a,a₁-dioxypyridines or glutaconimides:

I.
$$CH \stackrel{CII-C(OH)}{\sim} N$$
 II. $CH \stackrel{CH-CO}{\sim} NH$ III. $CH \stackrel{CH-CO}{\sim} NH$.

(Compare the pyrazolons, the isoxazolons, benzimidazolons, indoxyl, isatin, etc.)

(1) Monoxypyridines: 1-Oxypyridine, a Pyridone, Calloon, melting at 1060 and boiling at 281°, is obtained from oxyquinolinic acid (p. 537) and from oxy-nicotinic acid. Bromine water converts it into a dibromoxpyridine, C₈H₂Br₂(OH)N, melting at 206°. With ethyl iodide it yields n-ethyl-a-pyridone, CH CH = CH boiling at 247°, while the silver salt of a-oxypyridine and the same reagent yield a-ethoxy-pyridine, CH \sim CH \sim CH \sim N, boiling at 156°. a-Methoxypyridine can also be prepared from a-pyridone and diazomethane (p. 445; B. 28, 1625).

1,3 Dimethyl-a-pyridone, Pseudolutidostyril, Mesitene Lactam, melting at 180°, results from the action of ammonia upon dimethyl coumalin or mesitene lactone (p. 522), as well as from its carboxylic acids (1, 363). a-Phenyl Pyridone, melting at 107°, is formed from phenyl coumalin and ammonium acetate. With aniline it yields a,n-di-

phenylpyridone, melting at 145° (B. 29, 1677).

2 Oxypyridone, C₅II₄(OII)N, melting at 124°, distils without decomposition. It is produced when 3 pyridine sulphonic acid is fused with caustic potash (B. 28, R. 911), or by the action of nitrous acid upon β-amidopyridine. Its ethyl ether, C₅H₄(OC₂H₅)N, results from the interaction of β -brompyridine and alcoholic potash.

3 Oxypyridine, γ -Pyridone, $C_5H_5ON(+H_2O)$, melting at 148°, is produced by heating oxypicolinic acid and ammon chelidonic acid. Methyl iodide converts it into the hydroiodide of n-methyl-y-pyridone, OC < CH = CH > NCH₂, melting at 89°.

γ-Methoxy-pyridine, (CH₃(1))CCH = CH N, is isomeric with it. This compound may be prepared by heating γ-chlorpyridine with sodium ethylate. It boils at 190°,

and, unlike its isomeride, is broken down, when heated with hydriodic acid, into methyl iodide and pyridone.

2,4-Dimethyl-3-oxypyridine, γ -Lutidone, $C_5(CH_3)_3H_3ON(+ 1½H_3O)$, melting at 225°, is obtained from lutidone dicarboxylic acid (p. 538), as well as from dihydracetic acid (p. 521) on heating with ammonia (B. 28, R. 644). γ -Ethoxylutidine, boiling at 207°, results upon diazotizing ; amidolutidine (p. 533) in alcoholic solution (B. 27, 1328).

(2) Dioxypyridines: 1,5-Dioxypyridine, glutaconimide, C₈H₆O₂N (1, 467), melting at 183-184°, is obtained from oxyglutarimide, glutaconamic acid, or glutacondiamide. Its salts (chloride, + H₂O; sulphate, + 211₂O) are decomposed by much water. It yields pyridine upon distillation with zinc-dust. Phosphorus pentachloride converts it

into pentachlorpyridine (compare p. 527).

2-Methyl-1,5-dioxpyridine, C₅(CH₃)H₄O₄N, melting at 191°, 2-Ethyl-1,2-Benzyldioxypyridine, etc., have been prepared by the action of ammonia upon methyl-, ethyl-, and benzyl-glutaconic esters (B. 26, R. 318, 587). These dioxypyridines correspond to resorcinol of the benzene series, and like it they form dyes with phthalic anhydride (see p. 364 and B. 26, 1559).

Consult B. 25, R. 793; 28, R. 644, for 1,3-dioxypicoline.

Different isomeric dioxypyridines have, furthermore, been prepared by the fusion of

pyridine disulphonic acids with caustic potash (B. 17, 1832) and by the removal of CO₂ from comenamic or dioxypicolinic acid (p. 538) (B. 18, R. 633), etc.

(3) Trioxypyridines: 1,3,5-Trioxypyridine, Triketopiperidine, C₅H₅O₃N, decomposes at 220-230°. It corresponds to phloroglucin (p. 165). It can be obtained by boiling glutazine with hydrochloric acid. Heated with ammonia it reforms Glutazine, β-Imidoglutarimide, NH: C CH, CO NH (?), melting with decomposition at 300°, which

may be prepared by heating acetone dicarboxylic ester with ammonia (B. 20, 2655). Pyromecazonic Acid is an isomeric trioxypyridine, obtained from pyromeconic acid

with ammonia. Ferric chloride colors it a dark indigo-blue.

They arise (1) 7. Pyridyl Alcohols: These are sometimes called pyridyl alkines. in the aldol condensation of a-methyl pyridines with aldehydes on boiling with water; (2) from their HBr-esters, the homologous pyridines brominated in the side-chain; (3)

by the reduction of the corresponding ketones:

1-Picolyl Alkine, C₅H₄NCH₂(CHOH)CH₃, are obtained from a-picoline with formic and acetaldehydes (B 22, 2583; 23, 2709, 2725).

1-Picolyl Trichlor-methyl Alkine, C₄H₄NCH₂(CHOH)CCl₃, melting at 87°, is formed from a-picoline and chloral. Alcoholic potash converts it into a pyridyl acrylic acid (p. 538). Pyridyl-a-ethyl Alkine, C₄H₄NCH(OH)C₄H₅, boiling at 213° to 218°, is isomeric with a-picolylmethyl alkine. It is made by reducing pyridyl ethyl ketone with sodium amalgam. 1-Picolyl-4-methyl Alkine, C₅H₃(CH₂)NCH(OH)CH₂, boiling at 240°, results upon boiling bromcollidine with water (B. 28, 1759).

8. Pyridyl Ketones: Ketones of the pyridine series are obtained in the distillation

of pyridine carboxylic acids with fatty or aromatic acids (Engler, B. 24, 2525).

yield secondary alcohols, together with pinacones, by reduction.

1-Pyridyl Methyl Ketone, (CH₃CO)C₅H₄N, boiling at 192°, is prepared from calcium picolinate and acetate. Its oxime melts at 120°. Its phenylhydrazone melts at

2-Pyridyl Methyl Ketone, boiling at 220°, is obtained from calcium nicotinate and

acetate. I-Picoline-4-methyl Ketone, C₅H₅(CH₃)(COCH₃)N, boiling at 233°, results upon oxidizing the corresponding alkine (B. 28, 1764).

I-Pyridyl Ethyl Ketone, (C₂H₅CO)C₅H₄N, boiling at 205°, is changed by sodium and amyl alcohol to a-thyl piperyl alkine, C₂H₅CH(OH). C₅H₉NH, which is identical

with the pseudoconhydrin, present in the conine alkaloids.

- 2-Phenyl Pyridyl Ketone, C_6H_6CO . C_5H_4N , boiling at 307° (B. 20, 1209), forms two isomeric oximes, melting at 142° and 162° (B. 29, R. 832). β , Diacetyl-a, alutidine, $C_5H(COCH_3)_3(CH_3)_3N$, is produced by the action of ammonia upon methenyl-bisacetylacetone, $(CH_3CO)_2CH$. CH: $C(COCH_3)_3$ —compare 1, 478). I-Acetacetyl Pyridine, $(C_5H_4N)CO$. CH_2 . CO. CH_3 , melting at 50° and boiling at 137–143° (15 mm.), is obtained from picolinic ester, acetone, and sodium ethylate (B. 29, R. 846).
- 9. Pyridine Carboxylic Acids.—These acids of pyridine result upon oxidizing the homologous pyridines with potassium permanganate, when alkyl as well as phenyl groups are converted into carboxyl. condensed pyridine derivatives—e. g., quinoline, isoquinoline, etc.—are similarly decomposed, the benzene rings being ruptured and oxidized to carboxyl. Hence, most alkaloids, being pyridine derivatives, yield these acids upon energetic oxidation.

The lower acids can be prepared from the pyridine polycarboxylic acids by heating them with hydrochloric acid. Usually, in this treatment it is the COOH groups, occupying the a-position, which are split off. Upon heating with lime all the carboxyl groups are eliminated and pyridine is formed.

The pyridine carboxylic acids, like the other pyridine derivatives, are reduced by sodium and alcohol to piperidine carboxylic acids.

A number of pyridine carboxylic acids are reduced by sodium amalgam in aqueousalkaline solution to lactonic acids of the fatty series. The group—CH = N—CH = is then converted into—CO—O—CH,—(B. 25, R. 904; 25, R. 8; 27, R. 193, etc.).

As the pyridines are bases, their acids manifest the character of amido-acids. The

basic properties disappear with the polycarboxylic acids.

The methods of determining position or place in the monocarboxylic acids have been given on p. 531. Of the dicarboxylic acids, quinolinic acid, because of its formation from quinoline (p. 527), must be the a, 3-dicarboxylic acid, and cinchomeronic acid, because of its production from isoquinoline (p. 554), must be the β , γ -dicarboxylic acid.

A. Pyridine-mono-carboxylic Acids:

1-Pyridine Carboxylic Acid, Picolinic Acid, C₅H₄N(CO₂H), is obtained by the oxidation of a picoline. It melts at 135-136°, and sublimes. Ferrous sulphate imparts to its solutions, as well as to those of all pyridine carboxylic acids having the carboxyl group in the a-position, a yellow-red color.

2 Pyridine Carboxylic Acid, Nicotinic Acid, was first obtained by oxidizing nicotine. It is also prepared from β -picoline, as well as from β -cyanpyridine. It melts

at 228-229°. Its iodmethylate forms a betaine, C5H4(COO)N. CH3, which is identical with the alkaloid trigonelline (p. 564). 5-Chlornicotinic Acid, melting at 199°, is obtained from oxynicotinic acid, and when heated with ammonia becomes 5-Amidonicotinic Acid, which changes to a-amidopyridine on heating, and by nitration yields 4,5-nitroamidonicotinic acid, melting at 280°. The reduction of the latter yields 4.5 diamidonicotinic acid. I-Amidonicotinic Acid, from quinolinamic acid, also yields a amidopyridine on the application of heat, and by nitration becomes nitroamido-

nicotinic acid (B. 27, 1317; A. 288, 253).

3 Pyridine-carboxylic Acid, Isonicotinic Acid, is obtained from methyl pyridine, or from cinchomeronic acid, by the splitting-off of CO₂. It melts at 304°.

Homologous Pyridine Monocarboxylic Acids:

3-Methyl I pyridine Carboxylic Acid is obtained on heating uvitonic acid when ICO2 splits off. It sublimes without previously fusing.

3 Methyl-nicotinic Acid results on heating methyl quinolinic acid. It melts at

1,3-Dimethyl-nicotinic Acid, C₅H₂(CH₃)₂N(CO₂H). Its ethyl ester results in the condensation of acetoacetic ester with aldehyde and aldehyde ammonia. The free acid contains two molecules of water of crystallization.

B. Pyridine Dicarboxylic Acids:

1,2-Pyridine Dicarboxylic Acid, Quinolinic Acid, C₅H₂N(COOH)₂, melting at 190° with decomposition, is obtained from quinoline and from 1- and 2-methyl-quinoline by oxidation with potassium permanganate (B. 19, 293). The oxidation of p-oxyquinoline with bleaching lime yields an intermediate product, carbopyridyl glyceric acid,

C₅H₅N COOH CH(OH)COOH, which changes with ease to acetonicotinic acid,

 $C_5H_3N < \frac{COOH}{COCH_3}$ (compare B. 26, 1501, and decomposition of β -naphthol and naphthoquinone, pp. 392, 393).

The anhydride melts at 134° and the imide at 230° (A. 288, 257).

2,3-Pyridine Carboxylic Acid, Cinchomeronic Acid, is obtained from cinchonine

and cinchonidine by oxidation with nitric acid and by the oxidation of isoquinoline with potassium permanganate. It melts at 266° with decomposition. It yields an anhydride, C₃H₂N(CO)₃O, melting at 67°. Sodium amalgam reduces it to cinchonic acid, C₃H₄O₅, which breaks up into CO₃, and hydrocinchonic acid or dimethyl maleIc anhydride on application of heat (B. 18, 2968; 1, 465).

The methyl betaine of cinchomeronic acid is Apophyllenic Acid.

1,3-Pyridine Dicarboxylic Acid, Lutidinic Acid, $C_5H_3N(COOH)_2 + 2H_2O$, melts at 235° (A. 247, 37). 1,4-Pyridine Dicarboxylic Acid, isocinchomeronic acid, crystallizing with 1-1½ mols. of water, melts at 236° (B. 19, 1311).

1,5-Pyridine Dicarboxylic Acid, Dipicolinic Acid, melts at 225° (A. 247, 33).

2,4-Pyridine Dicarboxylic Acid, Dinicotinic Acid, melts at 314° (B. 19, 286).

Homologous Pyridine Dicarboxylic Acids:

3-Methyl-quinolinic Acid, C₈H₂(CH₂)N(CO₂H)₂, is produced upon oxidizing y-methyl-quinoline with potassium permanganate. It melts about 186° with decomposition.

I-Methylpyridine 5,3 dicarboxylic Acid, Uvitonic Acid, C₅(CH₂)II₂N(COOH)₂,

is formed when alcoholic ammonia acts upon pyroracemic acid. It melts at 244°

Lutidine Dicarboxylic Acid, 1,5-Dimethyl-2,4-pyridine Dicarboxylic Acid,

C₈H(CH₃)₂N(COOH)₂, melting at 316°, is formed from methenylbisacetacetic ester and ammonia (compare 1, 483, and A. 241, 31).

(1,3,5)-Trimethyl-pyridine-(2,4)-dicarboxylic Acid, Collidine Dicarboxylic Acid, C₅(CH₂)₅N(CO₂H)₂. The diethyl ester is prepared by the oxidation of dihydro-collidine dicarboxylic ester in alcoholic solution with nitrous acid. It is the starting out substance

for the preparation of a series of higher and lower pyridine carboxylic acids.

C. Pyridine Tricarboxylic Acids: 1,2,3-Pyridine Tricarboxylic Acid, Carbo-cinchomeronic Acid, C₅H₂N(COOH)₃ + 1½H₂O, melting at 250°, results upon oxidizing quinine, cinchonine (p. 572), various decomposition products of these alkaloids, and y-methyl quinolinic acid, etc., with potassium permanganate. Consult C. 1897, 11, 308, 1,3,5-Pyridine Tricarboxylic Acid, melting with for the esterification of this acid. decomposition at 145°, is obtained from symmetrical collidine (p. 532) or from uvitonic acid (A. 228, 29). 1,3,4-Pyridine Tricarboxylic Acid, Berberonic Acid, obtained by the action of nitric acid upon the alkaloid berberine, melts at 235° (B. 25, R. 582).

1,2,5-Pyridine Tricarboxylic Acid, (+2H₁O), decomposes at 12,5° (D. 25, N. 582).

D. Pyridine Tetracarboxylic Acids: 1,2,3,5-Pyridine Tetracarboxylic Acid,
C₅HN(COOH)₄(+2H₂O), melting at 227°, is obtained from collidine carboxylic acids, or from flavenol (p. 546), a quinoline derivative (B. 17, 2927). Consult B. 19, 1309, for the 2,4,5 of the collisions.

for the 1,2,4,5-acid, etc.

E. Pyridine Pentacarboxylic Acid, C₅N(CO₂H)₅ + 2H₂O, decomposing at 220°, is formed by the oxidation of collidine dicarboxylic acids.

8. Oxypyridine Carboxylic Acids: The views expressed on p. 534 relative to the oxypyridines or pyridones apply to the constitution of the oxypyridine carboxylic acids. The latter are obtained with remarkable ease from the corresponding pyrone carboxylic acids by the action of ammonia. When heated they break down, as a rule, quite readily into carbon dioxide and pyridones.

A. Monoxypyridine Carboxylic Acids: 1-Oxypyridine-4-carboxylic Acid, Oxynicotinic Acid, C5H4ON(COOH), melting at 303°, is produced when ammonia acts upon coumalic acid ester, and by the elimination of carbon dioxide from oxyquinolinic acid.

1-Oxypyridine-2-carboxylic Acid, melting with decomposition at 255°, is made from 1-amidonicotinic acid (p. 536), and in various other ways (A. 288, 265; M. 9, 145).

3-Oxypyridine-1-carboxylic Acid, Oxypicolinic Acid, (+ H₂O), melting at 250°, is produced by the action of ammonia upon comanic acid (p. 522). I-Oxypyridine-4,5-dicarboxylic Acid, Oxyquinolinic Acid, C₅H₃ON(COOH)₂, decomposing at 254°, is obtained from quinolinic acid by the potash fusion, or from its methyl ether, methoxyquinolinic acid, melting at 140°, which results when potassium permanganate acts upon amidocarbostyril ether. 3-Oxypyridine-1,5-dicarboxylic Acid, Ammonchelidonic Acid, Chelidamic Acid, is obtained by the action of ammonia upon chelidonic acid (p. 522).

1,3-Dimethyl-5-pyridone Carboxylic Acid, Pseudolutidostyril Carboxylic Acid, $C_5(\text{CII}_3)_2\text{H}_3\text{ON}(\text{COOH})$, results upon heating HCl- β -amidocrotonic ester to 130° (B. 24, R. 632). n-Phenyl Lutidone Carboxylic Acid, $C_5\text{H}(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{ON}(\text{COOH})$, is similarly produced, together with γ -oxyquinaldine, upon heating β -anilidocrotonic ester. 1.5-Lutidone-2,4-dicarboxylic Acid, $C_5(\text{CH}_3)_2\text{HON}(\text{COOH})_2$, melting at 267°, results when ammonia acts upon dimethyl pyrone dicarboxylic ester. Pentachoride of phosphory connected in the connected in t phorus converts it into 3-chlorlutidine dicarboxylic acid, melting at 224°, which yields 3 amidolutidine dicarboxylic acid with ammonia at 130° (B. 27, 1323

B. Dioxypyridine Carboxylic Acids: Dioxypicolinic Acid, C₅H₄O₂N(COOH).

Comenamic Acid, is derived from comenic acid (p. 522) by aid of ammonia.

1,5 Dioxyisonicotinic Acid, Citrasinic Acid, is formed when citramide, CONH,C (OH) < CH₂ CONH₂, is heated with concentrated sulphuric acid.

An aldehyde dicarboxylic acid, $C_5H_2O_2N(COOH)_2(CHO)$ (B. 29, R. 1105), is obtained in the action of chloroform and caustic potash upon citrazinic acid.

9. Pyridyl substituted acids of the fatty series are not very numerous. Certain pyridyl

lactic acids, because of their relations to the alkaloids, have been investigated:

lactic acids, because of their relations to the alkaloids, nave been investigated:

a, 2-Pyridyl Lactic Acid, C₅H₄N. C(OH)(CH₂)COOH, is formed, along with tribronide converts it into pyridyl brompropionic acid, C₆H₄NCBrCH₂. COOH. The homologous picoline-a-lactic acid, [C₅(CH₂)H₂N]C(OH)(CH₂)COOH, is obtained by saponifying its nitrile, the cyanhydrin of picolylmethylketone (p. 535) (B. 28, 1765).

β, 1-Pyridyl-lactic Acid, C₆H₄N. CH₂CH(OH)COOH, melting at 125°, is prepared by decomposing its ortho-chloride, trichlormethyl picolylalkine, C₆H₄NCH₂CH(OH)CCl₁ (p. 525), with scala, whereas with alcoholic potash the product is— (p 535), with soda, whereas with alcoholic potash the product is—
Pyridyl-a-acrylic Acid, C₈H₄N. CH: CH. COOH. Bromine converts this acid into

pyridyldibromprepionic acid, and hydrobromic acid changes it to pyridylmonobromepropionic acid, C₅H₄, CHBr. CH₂, COOH (A. 265, 221). a,2-Picoline Acrylic Acid, [C₆(CH₃)H₅N]CH(: CH₂)COOH, is obtained from picoline brompropionic acid, the

reaction product of PBr, and picoline lactic acid.

HYDROPYRIDINE DERIVATIVES.

Hydropyridines, and, indeed, the perhydrogenized products,—the piperidines,—are produced when the pyridines are reduced with zinc and hydrochloric acid, or, better, with sodium and boiling alcohols, and by electrolysis (B. 29, R. 1122; C. 1897, I, 388).

a. Hantzsch obtained dihydropyridine derivatives in the pyridine syntheses from acetoacetic ester and aldehyde ammonias. They part very readily with two atoms of hydrogen and revert to pyridines. Further, several dihydropyridines have been obtained as liquids with penetrating odor and easily resinified, by the action of caustic potash upon alkylpyridinium iodides (B. 14, 1497).

b. Tetrahydropyridines, Piperideines: Tetrahydropicoline, C, H, (CH,)N, boiling at 132°, is obtained from d-amidobutylmethyl ketone by ring formation (B. 25, 2190 ;

A. 294, 135):

The tetrahydropyridines include a series of bases, which have been prepared from the piperidines by the action of bromine and sodium hydrate, or iodine and silver oxide, or by the exit of water from the oxypiperidines. Thus, the coniceines result from the

action of phosphorus pentoxide upon conhydrin (p. 562).

The n alkyl derivatives of the pyridones (p. 534) and the dioxypyridines or glutacon-imides are to be viewed as keto-derivatives of di- and tetrahydropyridines.

c. Hexahydropyridines, Piperidines: Hexahydropyridine, Piperidine, Pentamethyleneimide, $CH_1 - CH_1 - CH_1 > NH$, boiling at 106°, is

dissolving quite readily in water and in alcohol. Its odor is like It occurs attached to piperic acid (p. 285) as piperine in , and is produced when piperine is heated together with alcoholic It may be synthesized (1) by heating pentamethylene diamine :hloride; (2) by heating ε-chlor- and ε-bromamylamine with caustic (previously mentioned); and (3) by the reduction of pyridine, hich it passes when heated with sulphuric acid to 300°, or, better, itrobenzene to 260°, or by boiling with silver oxide or silver : in glacial acetic acid (B. 25, 1620).

mposition of Piperidine.—The piperidine ring is ruptured in the following hen piperidine (1) is heated to 300° with hydriodic acid it is converted into am-

nd n-pentane.

ben piperidine is oxidized with hydrogen peroxide it changes to δ -amidovaleric e (3) and n-glutarimide (4). The decomposition by means of hydrogen perith the formation of δ -amidoaldehydes is observed also with the homologous nes. The δ -amidoaldehydes regenerate the piperidines with caustic potash, and lium bisulphite form piperidine sulphonic acids (B. 28, 1459, 2273).

itric acid oxidizes piperidyl urethane (5) to γ-carbethoxyl-amidobutyric acid (6),

ields y-amidobutyric acid or piperidic acid with caustic potash.

**xassium permanganate oxidizes benzoyl piperidine (7) to δ-benzoyl-amido-n
**acid (8), which is changed by caustic potash to δ-amido-n-valeric acid (9) or peridic acid (B. 17, 2544)

peridine and methyl iodide form dimethylpiperidinium iodide (10), which moist tide converts into dimethylpiperidinium hydroxide (II). This breaks down, on on, into dimethylpiperidine, the Δ_4 pentenyldimethylamine (12) and water. If myldimethylamine be converted into Δ_i -pentenyltrimethylaminonium hydroxide in the latter be distilled, it will break down into piperylene (1, 99) or [1,4-pen-(14), trimethylamine, and water (A. W. Hofmann, Ladenburg, B. 16, 2058; the decomposition of the pyrrolidines, p. 461). The diagram affords a review receding decomposition-reactions:

Piperidine, being an imide base, is capable of forming a nitroso-compound, n-alkyl-

and n-acid-derivatives:

Nitrosopiperidine, C₂H₁₀N. NO, boiling at 218°, results from the action of nitrous acid upon piperidine. By reduction it becomes Piperylhydrazine, C₂H₁₀N. NH₁₀ boiling at 146°. See B. 30, 535, for the electrolytic reduction of nitrosopiperidine and the formation of dipiperidyl. n-Methyl Piperidine, C₅H₁₀N. CH₂₀ boils at 107°. n-Ethyl Piperidine boils at 128°. n,y-Brompropylpiperidine and trimethylene piperylium bromide, C₃H₁₀: NBr< $\frac{\text{CH}_2}{\text{CH}_2}$ >CH₃. See B. 29, 2389.

The great reactivity of piperidine with brom- and iod-benzenes, resulting in the pro-

duction of n-phenylpiperidine (B. 21, 1921), is very peculiar. This power is very manually and the phenylpiperidine (B. 21, 1921), is very peculiar. terially reduced in the case of a methyl piperidine (B. 23, 1388).

n-Phenyl Piperidine, $C_8 H_{10} N C_6 H_6$, boils at 250°. n-a- and β -Naphthyl Piperidine, boiling at 215° and melting at 56°, are obtained without difficulty from the naph-

thols and piperidine (B. 29, 1175).

n-Acetyl Piperidine, C₅H₁₀NCOCH₂, boils at 226°. n-Benzoyl Piperidine, C₅H₁₀NCOC₆H₅, melting at 48°, condenses when heated with benzaldehyde to dibenyl-pyridine (p. 532). Piperidyl Urethane, C₆H₁₀NCO₂C₆H₅, boils at 211°. The oxidation of benzoyl piperidine and piperyl urethane leads to the rupture of the piperi-

dire nucleus. See p. 539. Piperine, the alkaloid, is the piperide of piperic acid.

The homologous piperidines result when the homologous pyridines are reduced with sodium and alcohol. They are called pipecolines, C₃H₉(CH₃)NH, lupetidines, C₅H₁(CI_{1,3},NH, copellidines, C₅H₆(CH₃)(C₂H₅)NH, etc. (compare B. 28, 2270.)

The alkyl piperidines contain asymmetric carbon atoms, hence different members of this class of bases have been decomposed, by means of their bitartrates, into optically active components—c. g., a pipecoline (B. 29, 43, 422), the copellidine, boiling at 163° (B. 29, 1959), obtained from aldehyde collidine, and β -propyl piperidine, boiling at 174° (B. 30, 1060), isomeric with conine, which has been synthetically prepared from ε -chlor- β -propylamylamine.

a, a₁-Diphenyl Piperidine melts at 69° (B. 30, 1499).

n. Methyl-a-pipecolyl Alkine, C₅H₉[CH(OH)CH₃]NCH₃, boils at 215°, and
n. Methyl-a-vinyl piperidine, C₅H₉(C₂H₃)NCH₃, boils at 162° (C. 1897, I, 386).

Triacetonamine and vinyl diacetonamine (1, 219) are keto-derivatives of the piperidine series:

$$\text{CO} < \begin{matrix} \text{CH}_2 - \text{C}(\text{CH}_3)_2 \\ \text{CH}_2 - \text{C}(\text{CH}_3)_2 \end{matrix} > \text{NH} \\ & \text{CO} < \begin{matrix} \text{CH}_2 - \text{CH}(\text{CH}_3)_2 \\ \text{CH}_1 - \text{CH}(\text{CH}_1)_2 \end{matrix} > \text{NH}.$$

They are produced in the action of diacetonamine upon acetone and benzaldehyde. The oxime of the vinyldiacetonamine, melting at 151°, yields upon reduction, depending upon the prevailing conditions, two stereoisomeric

7-Amidotrimethyl piperidines, $NH_3CII < \frac{CH_2 - CH(CH_3)}{CH_2 - C(CH_3)_2} > NH (a-body melting)$ at 26° and boiling at 84-86° (20 mm.); the β -body, an oil, boiling at 82-84° [22 mm.]). which nitrous acid changes to two stereoisomeric vinyldiacetonalkamines, or)-oxy-trimethyl piperidines, $C_5H_7N(OH)(CH_3)_3$, melting at 138° and 161°. The latter is rearranged by sodium amylate into the first (A. 294, 336). Sodium and alcohols reduce the pyridine carboxylic acids to piperidine carboxylic

Pipecolinic Acid, C₅H₁₀N(COOH), melting at 261°, is resolved by the bitartrates into d- and 1-pipecolinic acids, melting at 270° (B. 29, 2887). Hexahydroquinolinic Acid, C₅H₉N(COOH), has been obtained, similar to the hydrophthalic acids, in two stereo-isomeric forms, melting at 227° and 253°, of which each in the form of its nitrosocompound can be decomposed into two optically active forms (consult B. 29, 2665). Hexahydrocinchomeronic acid melts with decomposition at 256° (B. 29, 2187). Eucaine, derived from triacetonamine, is an oxycarboxylic acid derivative of the piperidine series. It is a tetramethyl-n-methyl-γ-benzoxypiperidine-γ-carboxylic ester, $(CH_3)N < \frac{C(CH_3)_2 - CH_2}{C(CH_3)_2 - CH_2} > C < \frac{OCOC_6}{COQCH_3}$, which has been recommended as a substitute for cocaine as an anaesthetic (C. 1896, 11, 709).

Conine, or a-propyl piperidine, tropine, and ecgonine are other important piperidine compounds. They are alkaloids or decomposition products of the latter. They will be discussed later, in the chapter relating to alkaloids.

Condensed nuclei, obtained from pyridine, have been prepared in great numbers, and are arranged in the following groups: II. Quinolines. III. Condensed Quinolines—
e. g., naphthoquinolines, anthraquinolines, phenanthrolines, quinoquinolines. IV. Isoquinotines. V. Phenanthridines. VI. Naphthyridines and Naphthinolines. VII.
Acridines (carbazacridines, quinacridines). VIII. Anthrapyridines. The alkaloids attach themselves as a distinct chapter to the preceding bodies.

II. QUINOLINE GROUP,

The quinoline bases, or benzopyridine group, occur with those of pyridine in bone oil (coal-tar), and are obtained by distilling different alkaloids with lime. The parent substance of the group was first obtained by Gerhardt (1842) from the alkaloids quinine and cinchonine.

As regards synthetic methods, transpositions, and isomerides, quinoline

is a naphthalene in which an a-CH-group is replaced by N.

This was first shown by synthesizing quinoline from allyl aniline. This is perfectly analogous to the synthesis of naphthalene from phenyl butylene (p. 390) (Königs):

$$\begin{aligned} \mathbf{C_6H_6.\,NH.\,CH_2.\,CH:CH_2} &= \mathbf{C_6H_6} \\ \mathbf{Allyl\,Aniline} & \mathbf{CH:CH_2} &= \mathbf{C_6H_6} \\ \end{aligned} \\ \mathbf{CH:CH=CH_2} \\ \mathbf{Quinoline.} \end{aligned}$$

A more direct proof of the constitution of quinoline was effected through its formation from hydrocarbostyril (p. 391); PCl₅ converts the latter into a dichloride, which upon heating with hydriodic acid yields quinoline (A. Baeyer, B. 12, 1320):

A "diagonal formula" has been suggested for quinoline because of its production in the distillation of acridine:

$$\bigcirc$$

Owing to the intimate genetic relations prevailing between the quinoline and pyridine derivatives we must assume for the pyridine nucleus of quinoline the same linkages as in pyridine itself (see p. 526). Furthermore, later researches upon the formation of quinoquinolines (p. 553) from quinolines afford additional proof against the "diagonal formula" (A. 273, 1).

Isomerisms of the Quinoline Derivatives:

We represent the three replaceable hydrogen atoms of the pyridine nucleus in quino-

line by a, β , and γ ; those of the benzene nucleus with 1, 2, 3, and 4.



The positions 1, 2, 3, referred to the N-atom, correspond to the ortho-, meta-, and parapositions of the benzene derivatives; 4 is known as the Assa-position. These positions are designated as the affinities of the benzene nucleus with o-, m-, p-, and a. Another nomenclature designates the affinities of the pyridine nucleus as Py-1, -2, and -3; those of the benzene nucleus as B-1, -2, -3, and -4. Consequently, seven mono-derivatives of quinoline are possible (B. 19, R. 443).

Syntheses of the Quinoline Derivatives:

1. The condensation of the ortho-amido-compounds of such benzene derivatives as have an oxygen atom attached to the third carbon atom of the side-chain.

In this way we obtain quinoline from o-amido-cinnamic aldehyde,

C₆H₄· NH₂· CH · COH, a-methyl-quinoline from o-amido-cinnamic methyl ketone, and a-oxy-quinoline (carbostyril) from o-amido-cinnamic acid.

2. The condensation of o-amidobenzaldehyde or o-amidobenzoketones with substances containing the group —CH₂—CO— (e. g., aldehydes, ketones, acetoacetic ester, malonic ester) to quinolines by means of sodium hydroxide is dependent upon the intermediate formation of such o amido-derivatives (Friedlander, B. 16, 1833; 25, 1752):

γ-Oxyquinolines are similarly formed from anthranilic acid (p. 211) with aldehydes, ketones, etc. (Ch. Zt. 17, Rep. 258; see also B. 28, 2809).

The synthesis of quinoline from o-toluidine and glyoxal and that of β -oxyquinaldine from o-toluidine and pyroracemic ester are similar (B. 27, 628; 28, R. 743):

$$C_6H_4 \stackrel{CH_3}{\searrow} + \stackrel{OCH}{\stackrel{OCH}{\longrightarrow}} C_6H_4 \stackrel{CH = CH}{\searrow} CH = CH$$

3. The production of quinoline and its derivatives substituted in the benzene nucleus by heating anilines with glycerol and sulphuric acid to about 1.40°, with the addition of nitrobenzene, or, better, arsenic acid (B. 29, 703) as the oxidizing agent. This method is of universal application, and can be very readily executed (Skraup):

$$C_6\Pi_5$$
. $NH_2 + C_3\Pi_8O_3 = C_6\Pi_4N(C_3H_3) + 3H_2O + H_3$.

Aniline Quinoline.

It is very probable that acrolein first results, this then combines with the aniline derivative yielding acrolein-aniline, which is oxidized to the quinoline derivative by the elimination of two hydrogen atoms by sulphuric acid. The halogen, nitro-, oxyanilines, toluidines, etc., behave similarly. The naphthylamines yield the naphthoquinolines; and the diamidobenzenes, the phenanthrolines.

Instead of using a mixture of the aromatic aniline and nitrobenzene, the corresponding nitro-body alone can be employed, which then is reduced in part by the hydrogen arising in the reaction. The first synthesis of this description was the preparation of alizarin blue (p. 554) from nitroalizarin (p. 427), glycerol, and sulphuric acid (A. 201, 333).

The following may be regarded as further generalizations of these syntheses:

4 (a). Quinolines substituted both in the benzene and pyridine nucleus are produced in the condensation of anilines with aldehydes, aided by sulphuric or hydrochloric acid (Quinaldine syntheses of Doebner and v. Miller). Aniline and acetaldehyde yield α-methyl quinoline or quinaldine:

$$C_6H_6$$
. $NH_2 + 2C_2H_4O = C_6H_4 < CH : CH
 $N : C(CH_3) + 2H_4O + H_2$

**Methyl Quinoline.$

All aldehydes of the formula CHO. CH, R react like acetaldehyde. The first step in the reaction consists in two molecules combining to unsaturated aldehydes, CHO. CR: CH. CH, R, or condensing to aldols corresponding to them. These then act upon the anilines and form quinoline bases with a CH₂-group in the a-position.

It is very probable that alkylidene anilines formed at first change to dimolecular, aldol-like condensation-products, which split off aniline and become quinaldines (B. 25, 2864; 29, 59; compare formation 2 of the indols, p. 466):

$$2CH_{8}.CH:NC_{8}H_{5} \longrightarrow \begin{array}{c} C_{6}H_{5}N:CH-CH_{2} \\ C_{6}H_{5}NH-CH.CH_{3} \end{array} \xrightarrow{C_{6}H_{6}NH_{2}} C_{6}H_{4} \xrightarrow{CH=CH} CH_{5}$$

The hydrogen set free sometimes occasions a partial reduction of the reaction-product

to tetrahydroquinoline derivatives (p. 550).

(b) Instead of two molecules of the same aldehyde, a mixture of two aldehydes, or an aldehyde with a ketone, may be used; in the latter case a, γ -di- or a, β, γ -trialkyl quinolines are formed (C. Beyer, B. 20, 1908)—e. g.:

$$C_{0}H_{5} \xrightarrow{CH_{3}} CO \cdot CH_{3} \xrightarrow{CH_{3}} CH_{5} \xrightarrow{CH_{3}} CH_{5} \xrightarrow{C} CH_{5}$$

$$C_{0}H_{4} + CHO \cdot CH_{3} \xrightarrow{C} CH_{5} \times CH_{5}$$

(c) a-Alkylcinchoninic acids (a-alkyl-quinoline-y-carboxylic acids) are produced by the interaction of a mixture of pyroracemic acid and an aldehyde upon aniline (p. 549) (B. 281, 1):

This is a reaction which, particularly when naphthylamine is substituted for aniline, proceeds so smoothly that the production of naphtho-cinchoninic acids may be applied as a test for the detection of aldehydes in mixtures. Pyroracemic acid alone, when heated with aniline, yields the a-methyl quinoline-y-carboxylic acid (aniluvitonic acid), together with phenyl lutidone; this is because aldehyde is formed from one molecule of the pyroracemic acid.

5. Oxyquinoline derivatives are obtained from aniline derivatives of β-ketonic acids and β-dicarboxylic acids by a ring formation (L. Knorr, B. 17, R. 147; A. 236, 112).

I

respective in the rest and the set amounts of when bested to Hoff, there is a rest of the comment and there is an enemy, principle prochylorogen to the comment and the commen

Not a financial to the same transment views it dimerity carbosynt and the mean in the mean accordance to mental pressionariosynthesis of the mean and another transmission directly the inflatest temperature, the mean and another when tented it had bloomed and Limpath, B. 4.

the set of the set of

The lases are lattices which dissolve with difficult and passess a penetrating lases, and like them form:

| The lattice are terriary lases, and like them form:
| The lattice are terriary saits, B. 28, R. 617). The

The state of the substituents present in the quinolines (B. 24,

the state of the sikyl minclinium iodides are unstable, just like the state of the sixth of the

$$\begin{array}{c} CH & \longrightarrow CH \\ CH_{\bullet} & CH$$

Magnificent blue dyes, the *Cyanines*, which, however, are unstable, and the constitution of which is not definitely known, are obtained by treating mixtures of alkyl quinolimium inclides and homologous alkyl quinolinium inclides with caustic potash (B. 18, R-171). When the quinolinium hydroxides are treated with alcohols, water splits off, and alcoholes (— $N < {CH_s \choose CH_s}$) remain.

3. Quinoline, like pyridine, is but slightly attacked by nitric acid or chromic acid. Potassium permanganate, however, destroys the benzene nucleus in them, with production of a,β -pyridine dicarboxylic acid (quinolinic acid, p. 536).

The homologous quinolines, containing the alkyl groups in the pyridine nucleus, and those containing the substituents in the benzene nucleus are oxidized by chromic acid in the presence of sulphuric acid to the corresponding quinoline carboxylic acids, while potassium permanganate, on the other hand, usually oxidizes those substituted in the benzene nucleus, with the formation of pyridine polycarboxylic acids (B. 23, 2252).

Potassium permanganate converts the a-alkyl quinolines, by the destruction of their pyridine nucleus, into acid derivatives of o-amidobenzoic acid. By this treatment a-phenyl quinoline yields bensoyl anthranilic acid (B. 19, 1196).

motine yields *bensoyl anthranitic acid* (B. 19, 1190). The pyridine nucleus is similarly ruptured by the oxidation of the quinolinium com-

nounds.

4. The pyridine nucleus of the quinolines, when reduced with zinc and hydrochloric acid, takes up four atoms of hydrogen, with the production of tetrahydroquinolines. Decahydroquinoline finally results by more energetic reduction.

The number of known quinoline derivatives is very great. To a certain extent they have a technical value as antiseptics, antipyretics, dyes, etc. Only the more important members of this group will receive consideration in the succeeding paragraphs.

Quinoline, C,H₇N, is a colorless, strongly refracting liquid, with penetrating odor, which possesses a powerful antiseptic action. It boils at 239°; its sp. gr. = 1.095 at 20°. It occurs in bone-oil and coal-tar. It results when many alkaloids are distilled, and is best prepared synthetically by Skraup's method—i. e., boiling a mixture of 38 grams aniline, 100 grams sulphuric acid, 24 grams nitrobenzene or arsenic acid, and 120 grams glycerol for several hours (B. 14, 1002; 27, 574; 29, 704).

It forms crystalline and very soluble salts with one equivalent of acids; the characteristic bichromate, (C₂H₇N₂)Cr₂O₇H₂, dissolves with

difficulty and forms yellow needles, melting at 165°.

Its iodmethylate, C₂H₁N. ICH₃, melting at 72°, is converted by sodium hydroxide into n-methyldihydroquinoline and n-methyl-a-quinoline.

Quinoline betaine, C₂H₁N. CH₂. CO. O, melts at 171°. Its hydrochloride is formed from quinoline and chloracetic acid. Di-, tetra-, hexa-, and decahydroquinoline result from the reduction of quinoline (p. 551).

Homologous Quinolines.—The seven isomeric methyl quinolines are all known. The four quinolines, methylated in the benzene nucleus, sometimes called toluquinolines or methylbenzquinolines, are obtained by the reaction of Skraup from the three toluidines: o-methyl quinoline boils at 248°, the para at 257°, the meta at 248°, and the ena at 250°.

a-Methyl-quinoline, Quinaldine, C, HaN(CH2), boiling at 247°, occurs in coal-tar (25 per cent.) (B. 16, 1082). It is produced by the various synthetic methods, by the reduction of γ-oxyquinaldine, and by fusing ethyl acetanilide, C₈H₈N(C₂H₈). CO. CH₈, with zinc chloride (B. 23, 1903). It may also be obtained by digesting aniline, paraldehyde, and crude hydrochloric acid for several hours (B. 16, 2465).

Chromic acid oxidizes it to a-quinoline carboxylic acid (see p. 545).

The CH₂-group of quinaldine is very reactive. It enters readily into condensation products with aldehydes (paraffin or benzene class) (B. 20, 2041). It combines with formaldehyde to a-oxethyl quinoline, which by loss of water forms a-vinylquinoline. C₃H₆(C₃H₃)N (B. 27, 2689). Chloral yields the compound, C₃H₆N. CH: CH. CCl₃, melting at 144°; boiling potassium carbonate converts it into a quinoline acrylic acid, C₂H₆N. CII: CH. CO₂H, while potassium permanganate oxidizes it to a quinoline aldehyde, C₂H₆N. CHO. Hydrobromic acid and soda convert quinoline acrylic acid into a quinoline-lactic acid (B. 21, R. 635; 28, R. 752). Consult B. 22, 271, upon quinoline acrylic acids and quinoline aldehydes. Quinaldine, oxalic ester, and sodium ethylate yield quinaldine oxalic acid, (C₃H₆N)CH₃. CO. COOH (B. 30, 1479). Quinaldine and phthalic anhydride yield a beautiful yellow dye—quinophthalone or quinoline yellow, $C_0H_4(C_2()_2)$: CH. N. C_0H_6 (p. 240), melting at 235°. The sodium salt of its sulphonic acid is the quinoline yellow of commerce. It dyes silk and cotton a beautiful yellow.

See B. 29, 187, for the action of quinaldine upon phthalaldehydic acids.

β-Methyl Quinoline, C_pH₆(CH₂)N (B. 20, 1916), boils at 250° and melts at 10-14°

y-Methyl-quinoline, Lepidine, occurs, together with quinoline and quinaldine, in coal-tar, and is obtained on distilling cinchonine with caustic potash. It may be synthetically prepared. It boils at 257°. Chromic acid oxidizes both methyl quinolines to the corresponding quinoline monocarboxylic acids. Potassium permanganate produces pyridine tricarboxylic acids.

a,3 Dimethyl Quinoline, C₉H₅(CH₃)₂N, boils at 261° (B. 22, 267).

a,y-Dimethyl Quinoline, boiling at 266°, is made from acetyl acetone and aniline, as well as from dihydrotrimethyl quinoline, which is produced by the interaction of indol and methyl iodide (p. 550).

 β, γ -Dimethyl Quinoline, from β, γ -dimethyl carbostyril, melts at 65° and boils at

290°. o- and p-Toluquinaldine, C₀H₅(CH₂)N (B. 23, 3483).

a-Ethyl Quinoline, C₀H₆(C₂H₆)N, boils at 255-260°, β-Ethyl Quinoline at 265°. They result on heating ethyl quinolinium iodide to 250° (analogous to the formation of alkyl pyridines, p. 528). γ-Ethyl Quinoline boils at 270-275°. Consult B. 21, R. 138, upon the trimethyl-quinolines.

a-Phenyl-quinoline, C9H6(C6H5)N, is obtained from cinnamic aldehyde and aniline upon heating them with hydrochloric acid to 200°. It melts at 84° and boils above 300°. Potassium permanganate oxidizes it to benzoyl anthranilic acid. β -Phenylquinoline is an oil, which solidifies on cooling (B. 16, 1836).

y-Phenyl-quinoline is formed from its acid. It melts at 61°. It is closely related to the quinia alkaloids (B. 20, 622). See B. 27, 907 (p. 571), for γ -Quinoline

Phenols.

Nitrophenyl Quinoline, NO₂C₆H₄. C₉H₆N, melting at 159°, is formed from iso-diazonitrobenzene and quinoline (B. 29, 168).

y-Phenyl-u-Methyl Quinoline, y-phenyl quinaldine, C,H5(C,H5)(CH3)N, results by the condensation of benzoyl acetone with aniline (B. 20, 1771). It melts at 99° and yields γ-phenyl quinoline a-carboxylic acid when its phthalone is oxidized with chromic acid. This new acid affords γ-phenyl quinoline.

a-Phenyl-y-methyl Quinoline is produced (B. 19, 1036) by distilling flavenol with

zinc-dust. It melts at 65°

Its p-amido-derivative, Flavaniline, applied as a beautiful yellow dye (B. 15, 1500), is a-Amidophenyl-7 methyl-quinoline, C₂II₅(CH₃)(C₄H₄NH₂)N. It results in the condensation of o-amido-acetophenone and p-amido-acetophenone when digested with zinc chloride (B. 19, 1038). Its monacid salts are yellow in color and have been used as dyes (B. 15, 1500). Nitrous acid converts it into so-called Flavenol, CaHa(CaHa- $OH_{\bullet}(CH_{\bullet})N$, a,p-Phenyl- γ -methyl-quinoline.

Various isomeric diquinolines, (C₀H₈N)₂, have been prepared by boiling quinoline with sodium; further, by conducting its vapors through tubes heated to redness, and finally from benzidine and other diamidodiphenylenes through Skraup's quinoline syn-

thesis (M. 8, 121; B. 17, 1965; 20, 634, etc.).

Diquinolyl Quinoline, C,H,N. C,H,N. C,H,N, melting at 151°, is formed from y-acetacetyl quinoline, C,H,N. COCH,COCH, (p. 549), with two molecules of o-amido-

benzaldehyde (B. 29, R. 845).

Triquinolyl Methane, CH(C₉H₆N)₂, melting at 202°, is obtained from pararosaniline by the reaction of Skraup (B. 24, 1606, 2267). Consult p. 357 for the opinion that

aldehyde green is a quinoline derivative.

Halogen, Sulpho-, and Nitro-derivatives of the Quinolines.—All those containing the substituents in the benzene nucleus are prepared by the methods in use for the introduction of such groups into benzene and naphthalene. Or the corresponding substituted benzene derivatives are subjected to the quinoline syntheses given on p. 544. difficult to introduce the halogens, the nitro- or the sulpho-groups into the pyridine nucleus of quinoline. Py-chlorine derivatives of quinoline are chiefly made by the action of PCl₈ upon py-oxyquinolines. The ready mobility of the halogen atoms occupying the a- or γ-positions in quinoline is very remarkable. They can be easily replaced by OH, NHR, etc.

a-Chlor-quinoline, C, H, ClN, melting at 38° and boiling at 267°, is prepared from carbostyril and PCI₈ (B. 15, 333). β -Chlor-quinoline, boiling at 255°, is produced from quinoline and sulphur chloride, along with the compound (C₂H₈N),S, and trichlor-quinoline (B. 29, 2456). a-Brom-quinoline melts at 49° (J. pr. Ch. [2], 41, 41). a-Brom-quinoline, melting at 13° and boiling at 276°, results from the action of sulphur bromide upon quinoline or by heating quinoline hydrochloride with bromine (B. 27, R. 732; 25, R. 422; 29, 2459).

y-Chlor-quinoline, melting at 34°, is obtained from kynurine and also from γ -amidoquinoline (B. 27, R. 748). γ -Brom-quinoline results when PBr_a acts upon kynurine (B. 27, R. 732). α -Iod-quinoline Iodmethylate, C₃H₆IN . ICH₃, melting at 212°, is produced when methyl iodide acts upon α -chlor-quinoline (A. 282, 376). α -Methyl β -chlor-quinoline, melting at 72°, is produced from methyl ketol, CCl₃H and sodium alcoholate (B. 21, 1942). α ₃ β -Dichlor-quinoline (B. 21, 1942). α ₃ β -Dichlor-quinoline (B. 21, 1942). α ₃ β -Dichlor-quinoline (B. 21, 1942). α ₄ β -Dichlor-quinoline (B. 21, 1942). α ₅ β -Dichlor-quinoline (B. 21, 1942). line, melting at 105°, results in the action of PCl₅ upon hydrocarbostyril. a,β,γ Trichlorquinoline, C9H4Cl3N, melting at 107°, is formed from malonanilic acid and PCl6 (B. 17, 737) (p. 544).

Amido-quinolines, substituted in benzene nucleus, are produced in the reduction of the corresponding nitroquinolines. The py-a- and y-amido-quinolines result upon heating a- or y-chlor- (brom-) quinolines with amines.

a-Amido-quinoline, C₂H₆(NII₂)N, melting at 114°, is produced by the reducing

decomposition of a-phenylhydrazide-quinoline, C₀H₆(NH.NHC₆H₆)N, the reaction product of phenylhydrazine and a-chlorquinoline. The oxidation of phenylhydrazido-

quinoline produces a-phenylazoquinoline, C₀H₆(N: NC₅H₅)N (B. 24, 2819).

a-Amidoquinoline Iodmethylate, C₉H₆(NI₃)N (B. 24, 2819).

a-Amidoquinoline Iodmethylate, C₉H₆(NI₃)N. ICH₃, melting at 247°, is formed directly from ammonia and a-iod-quinoline iodmethylate (A. 282, 380).

a-Phenylamido-quinoline, C₉H₆(NHC₆H₃)N, melting at 98°, results upon heating a-chlorquinoline and aniline to 200° (B. 18, 1532). y-Amido-quinoline, melting at 142-144° is formed when becoming and countries and co 142-144°, is formed when bromine and caustic potash act upon cinchoninamide (see amidopyridines, p. 533). y-Amido-quinaldine, C₂H₅(CH₃)(NH₂)N, melts at 270° (B. 21, 1980). p-Methoxy-y-amidoquinoline, C₂H₅(OCH₃)(NH₄)N, melting at 120°, results when potassium hypobromite acts upon the amide of quinic acid (B. 29, R.

Oxyquinolines.—The oxyquinolines manifest the character both of bases and of Those containing the hydroxyl in the benzene nucleus, called also quinophenols or oxybenzquinolines, are synthesized from the three amidophenols by Skraup's and Döbner-Miller's reactions; also by reduction of the Bz-nitroquinolines, or from the

quinoline sulphonic acids by fusion with caustic potash (B. 28, R. 912).

I-Oxyquinoline, C₈H₃(OH): (C₃H₃N), is most readily prepared from I-quinoline sulphonic acid (B. 16, 712). It melts at 75° and boils at 266°. From it is obtained **1-Ethoxy-4-acetamidoquinoline**, analgen, $C_8H_2(OC_2H_8)(NH.COCH_3):(C_3H_2N)$, melting at 155°, which has been recommended for the alleviation of pain. p.Oxyquino-

L

line, melting at 194°, results from the exit of carbon dioxide from xanthoquinic add

(p. 550).

The Bz-oxyquinolines, when acted upon in glacial acetic acid solution (Zincke's method), are converted, like the naphthols, into chlorinated quinoline-quinones, which (similar to the conversion of naphthalene derivatives into indenes) are rearranged to pyrindene-derivatives of a condensed pyridine and indene ring. Thus, from p-oxyquinoline and chlorine by various transformations of the primary reaction-products, dichlortriketotetrahydroquinoline (1) results. This, on boiling with water, becomes \(\beta\cdot\)-chlor-a-oxypyrindone (2), from which dichloracetopicolinic acid (3) is obtained by rupture of the ring (A. 290, 321):

$$(1) \ C_3H_3N < \begin{matrix} CO-CO \\ CO-CCI_2 \end{matrix} \longrightarrow (2) \ C_5H_3N < \begin{matrix} C(OH) \\ CO \end{matrix} \longrightarrow (3) \ C_5H_3N < \begin{matrix} COCHCI_4 \\ COOH \end{matrix} .$$

The oxyquinolines, with hydroxyl in the pyridine nucleus, are more feeble bases and phenols than the oxybenzquinolines. As in the case of the oxypyridines or pyridones (p. 534), it is undetermined whether the hydroxyl- or keto-form should be given to the oxyquinolines of the a- and y-positions. Ethers, however, of the two forms—e. g., carbostyril and pseudocarbostyril—exist:

a-Oxyquinoline, Carbostyril, $C_9H_7ON(+H_2O)$, the lactime or lactam of o-amido-cinnamic acid (p. 214), is most readily obtained by the reduction of o-nitro-cinnamic ester (B. 14, 1916). It may also be prepared from a-chlorquinoline by heating it with water, and by digesting quinoline with a bleaching lime solution (B. 21, 619). It melts at 199°.

Water decomposes its salts with alkalies and acids. Potassium permanganate oxidizes it to oxalyl anthranilic acid, $C_6H_4 < \stackrel{COOH}{NH}$. CO. CO₂H. Sodium and alcohol reduce it to tetrahydroquinoline.

Carbostyril Methyl Ether, boiling at 247°, and the ethyl ether, boiling at 256°, or a-methoxy- and ethoxy-quinolines, are oils. They are produced by the action of the alkyl iodides upon the Na- or Ag-salts of carbostyril, by the action of sodium alcoholates upon a-chlorquinolines, and when o-amidocinnamic esters are digested with alcoholic zinc chloride.

The pseudocarbostyril ethers—the methyl, melting at 71°; and the ethyl, at 54°—are produced by the action of the alkyl iodides upon free carbostyril in the presence of alkalies. Also when sodium hydroxide acts upon methyl- and ethyl-quinolinium iodide (p. 544). n-Methyl quinolon is also produced when ethoxyquinoline is heated with methyl iodide (B. 30, 930).

1-Nitrocarbostyril, C₉H₆(NO₂)ON, melting at 168°, results from the action of alcoholic ammonia upon nitrocoumarin.

3-Oxycarbostyril, melting beyond 300°, is formed by the condensation of 6-amido-m-coumaric acid, which is produced in the electrolytic reduction of o-nitrocinnamic acid.

y-Methyl-a-oxyquinoline, y-Methyl Carbostyril, or Lepidone, C₂H₆(CH₂)ON, melting at 223° and boiling at 270° (17 mm.), is obtained from acetoacetanilide (p. 544). Its lactime ether, a-Methoxy-y-methyl quinoline, boiling at 276°, results when NaOCH₃ acts upon a-chlorlepidine. The lactam ether: n-methyl lepidone, melting at 131°, is prepared from acetoacetic ester and methyl aniline (p. 543), and by heating ethoxylepidine with methyl iodide (B. 30, 931).

 β Oxy a methyl Quinoline, γ -Oxyquinaldine, $C_9H_6(CH_9)ON(+2H_2O)$, melting at 231°, from β anilido-crotonic ester (p. 543), also forms two isomeric ethers:

y-Methoxyquinaldine, boiling at 298°, and n-methyl quinaldone, melting at 175° (B. 22, 78). With methyl iodide both ethers yield the same todmethylate,

 $C(OCH_3) = CH$ C₆H₄<N(ICH₃) = C. CH₃, which upon heating or treatment with alkalies becomes n-methyl quinaldone (B. 30, 922). Compare the similar behavior of methoxyphenyl-

methyl pyrazole and antipyrine.

y-Oxyquinoline, Kynurine, C₉H₆(OH)N, is made by heating kynurenic acid (oxyquinoline carboxylic acid), and by oxidizing cinchonine and cinchoninic acid with chromic acid (B. 22, R. 758). It melts at 201°. PCl₅ converts it into y-chlorquinoline (B. 27, R. 748) (p. 547).

p,y-Dioxyquinoline, C₂H₂O₂N, results in the saponification of p-methoxykynurine, which is formed when nitrous acid acts upon p-methoxy-γ-amidoquinoline (B. 29,

R. 675)

a,y-Dioxyquinoline, C,H,O,N, sublimes. It is formed when caustic potash acts upon y-bromcarbostyril and upon digesting a-amidophenyl propiolic acid with SO₄II, (B. 15, 2151) (p. 284). The reduction of its β -nitroso-derivative produces a, β, y -trioxyquinoline, C. H.O.N, which ferric chloride oxidizes to quinisatinic acid (p. 261) and quinisatin or triketotetrahydroquinoline (B. 17, 985).

Quinoline Aldehydes and Quinoline Ketones:

a-Quinoline Aldehyde, C, H, (CHO)N, melting at 71°, is obtained from quinoline

acrylic acid (p. 546) with potassium permanganate.

Py-Quinoline ketones are produced by synthetic method 2 (p. 542) from o-amidobenz-aldehyde and β -diketones:

β-Acetyl Quinaldine, C₃H₅(CH₃)(COCH₃)N, melts at 57.5° (B. 25, 1756.) β-Acetyl Carbostyril, C₃H₅(COCH₃)ON, melting at 232°, is formed from o-amido-

benzaldehyde and acetoacetic ester (B. 16, 1838).

γ-Acetacetyl Quinoline, C₂H₇N(CO. CH₂. CO. CH₃), melting at 65° and boiling at 206° (17 mm.), is prepared from cinchoninic ester, acetone, and sodium ethylate. It condenses with phenylhydrazine to phenylquinolylmethyl pyrazole, melting at 120°, and with two molecules of o-amidobenzaldehyde to diquinoly! quinoline (p. 547; B. 29, R.

Quinoline Carboxylic Acids: They exhibit the character of amido-acids. substituted in the benzene nucleus have been synthesized from the amido benzoic acids (B. 28, 2809), and are produced when Bz-alkyl quinolines are treated with chromic acid. The Py quinoline carboxylic acids also result from the action of a chromic acid mixture upon Py-alkyl quinolines. The alkyl groups in the γ -position are most easily oxidized; the β - with more difficulty, and the alkyl groups in the a-position with the greatest difficulty (B. 23, 2254) (p. 544). When they are heated, carbon dioxide is expelled and the respective quinolines are produced. The acids, carrying the carboxyl in the a-position,

are colored reddish yellow by ferrous sulphate.
o-Quinoline Carboxylic Acid, CallaN(COOH), melts at 187°. The meta-acid melts at 248-250°. The para-acid melts at about 291°. The ana-acid melts at 360°

(A. 237, 325; B. 19, R. 443, 548).

a-Quinoline Carboxylic Acid, Quinaldic Acid, crystallizes from hot water in needles containing 2H,O; it melts at 156°, and decomposes. It is obtained from quinaldine.

β-Quinoline Carboxylic Acid is also produced by heating Acridic Acid. It melts

at 171°.

γ-Quinoline Carboxylic Acid, Cinchoninic Acid, was first produced upon oxidizing cinchonine with potassium permanganate or nitric acid. It contains I or 211,() (B. 20, 1609). It melts at 254°. It readily affords quinoline; potassium permanganate oxidizes it to a,β,γ-pyridine tricarboxylic acid.

a-Alkyl Cinchoninic Acids result from the condensation of aldehydes with pyroracemic

acid and anilines (B. 22, R. 23; A. 281, 1) (p. 543).

a-Methyl Cinchoninic Acid, Aniluvitonic Acid, CoH₅(CH₃)(COOH)N(+ H₂O), is obtained by the condensation of pyroracemic acid with aniline (p. 84) (B. 22, 1769). It melts at 240°, and breaks down.

a-Methyl-quinoline-β-carboxylic Acid results from the condensation of o-amidobenzaldehyde with acetoacetic ester (p. 543), and melts at 234° with decomposition.

Acridic Acid, a,β-Quinoline-dicarboxylic Acid, C,H,N(COOH), is produced when acridine is oxidized with potassium permanganate, just as quinoline yields a. 3 pyridine dicarboxylic acid. It crystallizes in needles with 2H₂O, or plates with 1H,O, and decomposes at 120-130°.

a, y-Quinoline-dicarboxylic Acid results when a-cinnamenyl-cinchoninic acid is oxidized with potassium permanganate (B. 22, 3009). It melts at 246° with decom-

Oxyquinoline Carboxylic Acids:

a-Oxyquinoline-3 carboxylic Acid, C,H,(OH)(COOH)N, results in the condensa-

tion of o amido benzaldehyde with malonic acid (p. 543) and melts above 320°.

a-Oxyquinoline-)-carboxylic Acid is formed on melting cinchoninic acid with potash. It melts at 310° and decomposes. Both acids decompose into CO, and carbostyril on heating their silver salts.

Kynurenic Acid is a y-oxyquinoline carboxylic acid. It occurs in the urine of dogs after the ingestion of meat. It contains 1H₂O and melts at 257°. Fusion with caustic

potash converts it into CO₂ and kynurine.

p-Oxyquinoline-y-carboxylic Acid, C₂H₅(OH)N(CO₂H)(+ H₂O), Xanthoquinic acid, results on fusing parasulphocinchoninic acid with KOH. It melts at 320° with decomposition. Its methyl phenol ether, Quinic Acid, C₂H₅(O. CH₃)N(CO₂H), is obtained by oxidizing quinine and quinidine with chromic acid in sulphuric acid solution. It melts at 280°.

 γ -Oxyquinaldine- β -carboxylic Acid, $C_9H_4(CH_1)ON(COOH)$, melting at 245° with decomposition, results in the condensation of anthranilic acid with acetoacetic ester (B. 27, 1396).

HYDROQUINOLINES.

Dihydroquinolines are obtained on treating alkyl quinolinium iodides with sodium hydroxide. Thus, the iodmethylate of cinchoninic acid yields n-methyl dihydrocinchoninic acid, C₆II₄: [C₃II₅(COOH)N. CII₃], along with n-methyl quinolon-y-car-boxylic acid (A. 282, 365; compare B. 25, 3326). These substances are, however, very easily altered.

Methyl iodide and trimethyl indol (p. 468) yield a base having the formula of a trimethyldihydroquinoline, C₉H₆N(CH₃)₃, boiling at 244°, which, however, upon the distillation of its iodmethylate again affords trimethyl indol, and by oxidation trimethyl indolinone (p. 471). It is reduced to a base having the formula of a trimethyltetrahydroquinoline, Cyll, N(CH3), which is also convertible into a dimethyl quinoline, but in other respects exhibits a behavior different from that of other tetrahydroquinolines (B. 29,

Ketodihydroquinolines or quinolons are the n-alkyl ethers of the oxyquinolines (p. 548).

Tetrahydroquinolines: These are produced when the quinolines are reduced with tin and hydrochloric acid, or with sodium and alcohol. The pyridine nucleus then takes up four hydrogen atoms. This procedure changes the chemical nature of the quinolines very materially. tetrahydroquinelines behave like secondary fatty-aromatic amines. Nitrous acid converts them into n-nitrosamines, which readily rearrange themselves to Bz.p-nitrosamines. With the salts of diazobenzene they yield diazoamido-compounds, which readily pass over into p-azophenyl derivatives. This alteration in the chemical character of quinoline is similar to that seen in the indols by their change to dihydroindols (p. 471). The tetrahydroquinolines are to be regarded as ring-homologues of the dihydroïndols:

urhereas the basal substances, the indols and the quinolines, behave very differently. The tetrahydroquinolines are oxidized to quinolines again chromic acid, silver acetate, or Hg(NO₃), (B. 27, 824).

Tetrahydroquinoline, C₂H₁₁N, boiling at 244°, is liquid at the ordinary temperature. **h** formed when tin and hydrochloric acid act upon quinoline and a- and γ -chlorquinones; also by the action of sodium and alcohol upon carbostyril (B. 23, 1142). Nitrous converts it into a nitroso-body, which is easily rearranged to p-nitrosotetrahydro-**Example 1** Into a nurso-body, which is easily rearranged to p-nursoiteralyaro-polinedine, melting at 134° (B. 16, 732). With benzoyl chloride it forms n-benzoyltetra-polinental number of the numb the action of a febrifuge.

Tetrahydrotoluquinoline, CH₃. C₄H₃: [C₃H₄N], boiling at 257°, is produced on **boiling toluidine** with trimethylene chlorobromide (B. 24, 2061; 25, 2805):

$$CH_{3}.\ C_{6}H_{4}NH_{3} + \frac{BrCH_{3}.\ CH_{3}}{ClCH_{3}} \xrightarrow{\hspace*{1cm}} CH_{3}.\ C_{6}H_{3} \stackrel{CH_{3}-CH_{2}}{\swarrow}$$

The nitreso-compound melts at 51°; the benzene-diazo-body at 99°.

in the reduction of o-nitrophenethylmethyl ketone, $C_6H_4 < \stackrel{NO_2}{CH_2}$, CH_2 , $COCH_3$ (B. 14, 890). It is changed to benzoylamido-phenylacrylic acid when its benzoyl derivative is oxidized. It has an asymmetric Catom, and by means of its bitartrate it is resolved into two optically active components (B. 27, 77). The \(\delta\)-lactams of o-amidophenyl fatty acids—\(\ella\). Hydrocarbostyril, or o-amido-phenylpropionic acid lactam, are keto-derivatives of tetrahydroquinoline. Hydrocarbostyril has been obtained by the Beckmann rearrangement of a-hydrindone oxime (p. 387), as well as from its acid, β -hydrocarbostyril carboxylic acid, $C_0H_{10}NO(COOH)$, melting at 146° with decomposition. Its ester results in the reduction of nitrobenzyl malonic ester (B. 29, 665). See pp. 253, 255, 256, for oxyhydrocarbostyril. Quinisatine, or o-amido-benzoyl gly-

oxylic acid lactam, is triketotetrahydroquinoline.

Hexa- and Decahydroquinolines: When quinoline or tetrahydroquinoline is heated to high temperatures with hydriodic acid and phosphorus, the benzene nucleus also takes up hydrogen, and the reaction-product yields, in addition to a little hexahydroquinoline,

CH₁₁N, boiling at 226° (B. 27, 1459), and other products:

Decahydroquinoline, C₂H₁₂N, melting at 48° and boiling at 204°. It is a very volatile, strongly alkaline substance, which has an odor astonishingly like that of conine.

While tetrahydroquinoline resembles the mixed fatty aromatic bases, decahydroquinoline manifests the properties of a secondary amine of the aliphatic series. It is the piperidine of the quinoline group:

When its bensoyl- and urethane-derivatives are oxidized, decahydroquinoline sustains decompositions similar to those of piperidine; the products are benzoylated o-amido-bexakydrophenylpropionic acid and the methyl urethane of o-amidohexahydrophenylacetic acid:

$$c_{gH_{10}} \leftarrow c_{H_{2}} - c_{H_{2}} - c_{gH_{10}} + c_{g$$

Free o-amidohexamethylenepropionic acid readily parts with water and becomes Decahydrocarbostyril, $C_0H_{10} < CH_2 - CH_2$ (p. 300) (B. 27, 1458).

Julole and lilole compounds are derivatives of hydroquinolines. They are probably derived from the hypothetical parent substances:



Lilole



Lilole must be considered as a combination of the quinoline nucleus with the pyrrol nucleus, or of the pyridine nucleus with the indol nucleus, while julole is a combination of the quinoline nucleus with the pyridine nucleus.

Diketomethyl Lilolidine, $CO-C_6H_3 < \stackrel{CH_9}{N-} > CH$. CH_9 , is obtained from malonic $CH_2 - CO$ ester and dihydromethyl ketol (p. 470). It has been described in connection with the

Ketomethyl Juloline, (CH₃)C—C₆H₃CH₂—CH₃, melting at 130°, is formed from HC ——— CO tetrahydroquinoline and acetoacetic ester (B. 24, 845).

Julolidine, CII,—C₆H₃ CH₂—CH₂, melting at 40°, is produced on boiling tetra-CH₃ — CH₃

hydroquinoline with one molecule of trimethylene chlorbromide, or aniline with two molecules of trimethylene chlorbromide (B. 25, 2801). Both julole derivatives are bases, whereas diketojulolidine, CO—C₆H₃—CH₂—CH₂, obtained from tetrahydro—CH₂—CO

quinoline and malonic ester, has only acid properties.

III. CONDENSED OUINOLINES.

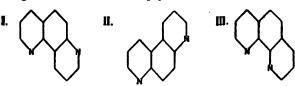
Condensations similar to those effected through aniline in the quinoline syntheses can be carried out with the higher aromatic amines—e. g., naphthylamine, anthramine, the amidoquinolines, the phenylenediamines, etc. All these amines yield with glycerol (Skraup), or with aldehydes, etc. (Döhner-Miller, p. 543), higher condensed bases, containing the quinoline nucleus.

In these reactions the pyridine ring, as a rule, then attaches itself only to two such members of the benzene nucleus, which, according to the requirements of the Kekulé formula, are doubly linked (B. 26, R. 402; 27, R. 631). This would argue against the various centric and diagonal formulas which have been suggested for the derivatives of benzene and of pyridine.

A. a- and β -Naphthoquinolines are obtained from both naphthylamines:

B. Anthraquinolines are formed from amidoanthracenes:

C. m- and p-Phenylenediamines yield phenanthrolines (I) and pseudophenanthrolines (II); a third isomeric phenanthroline (III) is obtained from o-amidoquinoline. For practical purposes these three isomerides may be distinguished as o-, m-, and p-phenanthrolines:



D. Quinoquinolines are obtained from the \gamma-amidoquinolines:



In their chemical behavior all of these bases resemble the quinolines.

A. a-Naphthoquinoline, $C_{13}H_9N$, melts at 52° and boils at 251°. β -Naphthoquinoline melts at 93°. The latter is obtained from the β -naphthylamines substituted in the a-position by bromine or NO2, through the splitting-off of the substituents. Potassium permanganate converts the naphthoquinolines into two phenylpyridine dicarboxylic acids (p. 531). The hydrides of the naphthoquinolines are noteworthy. In using tin and hydrochloric acid the pyridine nucleus, as in the case of quinoline, is hydrogenized:

Tetrahydro-(a)-naphthoquinoline, $C_{10}H_6 < \frac{CH_2 - CH_2}{NH - CH_2}$, melting at 46°, and the β -body, melting at 63°, behave like alkylic a- and β -naphthylamines. Sodium and boiling amyl alcohol produce ar-Octohydro-(a)-naphthoquinoline, $CH_3 - CH_2$ $CH_3 - CH_3$ $CH_3 - CH_3$ $CH_4 - CH_2$ $CH_5 - CH_2$ $CH_6 - CH_2$ $CH_6 - CH_2$ $CH_7 - CH_2$ $CH_8 - CH_2$

the \(\theta\)-compound, melting at 60° and boiling at 325° (717 mm.). In these bodies not only the pyridine nucleus, but also the outer benzene nucleus, has taken up hydrogen atoms, which accounts for their aromatic bensene amine-alkylic aniline-character. From β -naphthoquinoline there is simultaneously formed an isomeric ac-Octohydro- (β) -

decahydroquinoline and possesses the properties of a piperidine.

B. Anthraquinoline, C11H11N, melts at 170° and boils at 446°. Its solutions exhibit an intense blue fluorescence. Chromic acid oxidizes it to anthraquinone quino-

line, corresponding to anthraquinone. Its dioxy-compound is Alizarin Blue, Dioxyanthraquinone quinoline,

CH = CH $C_6 II_4 < CO > C_6 (OH)_2 < N = CH$, melting at 270°. It consists of metallic, bluish-

violet-colored needles. It is produced when m-nitro-alizarin or amido-alizarin is heated with glycerol and sulphuric acid (B. 18, 445; 29, 708). It unites with acids and bases to form salts. It occurs in trade in the form of a bluish-violet paste, and, like alizarin, is applied in dyeing. Since reducing agents decolorize it (zinc-dust, grape sugar) and it again separates on exposure to the air, it is adapted to the vat-dyeing.

By the action of sulphuric acid more hydroxyl groups are introduced into alizarin-blue. The products are alizarin-blue green, alizarin-green, alizarin-indigo-blue. These are mixtures of sulpho-acids of tri-, tetra-, and penta-oxyanthraquinone quinolines (B. 26,

R. 711).

C. (m)-Phenanthroline, C₁₂H₈N₂(+ 2H₂O), melting at (65°) 78°, is obtained from meta-diamidobenzene or 2-amidoquinoline (B. 16, 2519; 23, 1016). p-Phenanthroline, Pseudophenanthroline, is derived from p diamidobenzene or amidoazobenzene with glycerol and sulphuric acid. It melts at 173°. Potassium permanganate oxidizes the phenanthrolines to a,β - and β,β -dipyridyl dicarboxylic acids (B. 24, 2623).

a Methyl-o-phenanthroline, $C_{12}H_7(CH_3)N_2(+2H_2O)$, melting at (53°) 76°, is pre-

pared from 1-amidoquinaldine (B. 22, 253).

1). a-Methyl-γ-quinoquinoline, C₁₂H_γ(CH₂)N₂, melting at 206° and boiling at 360°, is prepared from γ-amidoquinaldine, glycerol, sulphuric acid, and nitrobenzene (B. 27, R. 632).

IV. ISOQUINOLINE GROUP.

While quinoline or benzopyridine results from pyridine by the attachment of the benzene nucleus to its carbon atoms occupying the α,β positions, the formula of the isomeric isoquinoline or isobenzopyridine is produced by the benzene nucleus joining itself to the β, γ -C-atoms of pyridine. Its nitrogen member is therefore separated from the benzene nucleus by a methine group:



Quinoline



Isoquinoline.

This constitution seems evident from the oxidation of isoquinoline to β, γ -pyridine dicarboxylic acid, as well as from the methods by which it is obtained synthetically.

Quinoline is similar to isoquinoline in its deportment. It is found with it in coal-tar (Hoogewerff and van Dorpp, 1885). It is the mother substance of a class of important alkaloids belonging to the opium bases -e. g., papaverine, narcotine, hydrastine, etc. (p. 578).

Syntheses of Isoquinoline Derivatives:

1. Isoquinolines are produced by ring-formation from benzene compounds of the constitution $C_6H_5-C-N-C-CO$ or $C_6H_5-C-C-CO$. For example, isoquinolines are formed on digesting benzylidene amidoacetal or benzylamidoacetaldehyde with sulphuric acid (B. 27, R. 628; 28, 764):

a-Methyldihydroquinoline (B. 26, 1904) is obtained from acetphenethylamide, C_6H_5 . CH_2 . CH_2 . $NHCOCH_3$. Trichlorisoquinoline is produced by the action of PCl_5 upon hippuramide, C_6H_5 . CO. NH. CH_2 . $CONH_3$, just as malonanilic acid, C_6H_5NH . CO. Cif. COOH, under like treatment yields trichlorquinoline (p. 547). The formation of isoquinoline from cinnam-aldoxime and from benzylidene-acetoxime upon heating them with P_2O_6 is remarkable (B. 27, 2795; 28, 818). It will be necessary to assume here an atomic rearrangement similar to that in the Beckmann transposition:

$$C_6H_6CH:CH:CH:N:OH \longrightarrow [C_6H_5:CH:CH:NH:COH] \longrightarrow C_6H_4 \stackrel{CH}{\swarrow} CH = CH$$
Cinnam-aldoxime

Cinnam-aldoxime

Cinnam-aldoxime

2. The linking oxygen atom in the lactones of the formula $C_6H_4 < CO - 0$, so-called isocoumarins, can readily be exchanged for the NH-group by means of cold aqueous ammonia. The products are isoquinolines or isocarbostyrils, which by successive treatment with PCl₅ and HI and phosphorus, or with zinc-dust, are converted into isoquinolines. Homophthalides and homologous homophthalides, under similar treatment, are also changed to isoquinolines (B. 21, 2299; 25, 1138, 1493, 3563; **26,** 1842):

Isoquinoline, C,H,N, melting at 23° and boiling at 240.5°, is very similar to quinoline. It occurs, together with ordinary quinoline, in the crude quinoline from coal-tar. It is separated from the accompanying compounds by the crystallization of the sulphates (B. 18, R. 384). In addition to the methods given above it is also produced by distilling benzylidine ethylamine, C.H. CH: N. CH. CH, through tubes heated to redness (B. 25, 734). Potassium permanganate oxidizes it to phthalic acid (destroying the pyridine nucleus) and β,γ -pyridine dicarboxylic acid (by destroying the benzene nucleus).

Alkylic phthalic acid imides are produced from the halogen alkyl addition products of

Its iodine (B. 21, R. 786).

Its iodinethylate, C₂H₁N. ICH₃, melting at 159°, is changed, like the quinolinium and pyridinium iodides (p. 530), by potassium ferricyanide and sodium hydroxide into n-methyl isoquinolon (B. 26, R. 270). Nitric acid changes isoquinoline into a Bz-nitroisoquinoline, melting at 110° (B. 29, R. 792). 2,3-Methylene Dioxyisoquinoline, (CH₃O₃)C₃H₃(C₃H₃N), melting at 124°, is obtained from piperonal acetalamine,

and upon reduction yields tetrahydro-2,3-methylenedioxyisoquinoline or hydrohydrastinine (p. 578; A. 286, I).

Bz-I- and 3-Methyl Isoquinolines, boiling at 2580 and melting at 830, and boiling at 264°, are prepared from o- and p-methylbenzylidene amidoacetal (C. 1897, I, 865).

a-Methyl Isoquinoline, C₅H₅(CH₅)N, boiling at 248° (its sulphate at 247°), results from the action of sulphuric acid upon acetophenone amidoacetal (B. 27, R. 628). It is probably identical with the methyl isoquinoline isolated from papaveroline (B. 23, R. 653). β-Methyl Isoquinoline, melting at 68° and boiling at 246°, is produced when methyl isocarbostyril is distilled with zinc-dust. γ-Methyl Isoquinoline, boiling at 256° is formed when dimethyl homophylholimida is distilled with zinc dust. 250°, is formed when dimethylhomophthalimide is distilled with zinc-dust (B. 21, 2300). 3-Ethyl Isoquinoline, C₃(C₄H₅)H₆N, boiling at 256°, and β-Phenyl Isoquinoline, C'₉(C'₆H₅)H₆N, melting at 104°, are obtained from ethyland phenyl-isocarbostyril (B. 25, 3573; 27, 2237). a-Phenyl Isoquinoline, melting at 88°, is derived from benzophenone imido-acetal, (C₆H₅)₂C: NCH₂CH(OC₂H₅)₃ (C. 1897, I, 865).

A beautiful red dye—Quinoline Red—is produced by condensing benzotrichloride with mindo-acetal condensing benzotrichloride and the state of the

with quinaldine and isoquinoline when they are heated with zinc chloride. This compound has a constitution analogous to that of malachite green (B. 20, 4).

In addition to its coloring properties, it possesses the remarkable power of rendering

photographic plates orthochromatic.

Isoquinolines, with halogens in the pyridine nucleus, result when PCl, acts upon the isocarbostyrils (below) and homophthalimides (p. 244). Chlorine atoms in the a position have the same reactivity as the chlorine atoms in the a- or γ-position of quino-

a position have the same reactivity as the cashing at 281°, is produced by the line (p. 547).

β-Chlorquinoline, C₉H₆ClN, melting at 48° and boiling at 281°, is produced by the partial reduction of a,β-dichlorisoquinoline, C₉H₆Cl₂N, melting at 122° and boiling at 366°, which is produced on treating homophthalimide with POCl₃ (B. 19, 2355).

a Chlor-β-methyl and a-Chlor-β-phenyl Isoquinolines, melting at 36° and 77°, are obtained from the corresponding isocarbostyrils. The latter combines with aniline to a-Anilido-β-phenyl Isoquinoline, C₂H₅(NHC₆H₃N), melts at 126° (B. 25, 2709).

Oxvisoquinolines, isocarbostyrils, are metameric with the carbostyrils (below). result from the action of ammonia upon isocoumarins (p. 555). Another universal method of producing the i-ocarbostyrils consists in rearranging the reaction products of acid anhydrides and o-cyanbenzyl cyanide (p. 286) with alkalies:

The alkyl cyanisocarbostyrils produced in this way are readily decomposed by concentrated sulphuric acid. The cyanogen group is eliminated and β -alkylic isocarbostyrils result (B. 27, 827, 2232; 29, 2543).

Isocarbostyrils, like the carbostyrils, yield ethers of the hydroxyl and keto-forms. The latter are obtained from isocarbostyrils and alkyl iodides, while the former are mostly made through the interaction of a-chlorisoquinolines and sodium alcoholates.

Isocarbostyril, a-Isoquinoline, C_pH₁ON (p. 286), results from isocoumarin and ammonia, and from isocarbostyril carboxylic acid, C_pH₂ON.COOH, a reactionproduct of ammonia and isocoumarin carboxylic acid, by the elimination of CO₂.

a Methoxyisoquinoline, C_6H_4 CH = CH boiling at 240°, is produced by the interaction of the silver salt of isocarbostyril and methyl iodide. The isomeric n-Methyl-a-isoquinoline, C_6H_4 $CO = N(CH_3)$, melting at 54° (40°: B. 26, R. 270; 27, 205), is obtained from isocarbostyril, methyl iodide, and alkalies (B. 26, R. 236), or by the action of alkaline potassium ferricyanide upon methyl isoquinolinium iodide (p. 555); other n-alkyl isoquinolons are produced by the action of primary amines upon isocoumarin (B. 27, 198), or its carboxylic acid. β -Methyl Isocarbostyril, $C_s(CH_s)H_{g}$ -ON, melts at 211°; β ethyl isocarbostyril melts at 141°; β isopropyl isocarbostyril

melts at 221° (B. 29, 2393). β -Phenyl Isocarbostyril, isobenzal phthalimidine, melting at 197°, also results from the action of ammonia upon isobenzalphthalide (B. 18, 2448; 27, 2237).

2448; 27, 2237).

A bz-2,3,4-Trioxy-γ-methyl Isocarbostyril, C₄H(OH)₃: [C₄H₄(CH₃)ON], is derived from the corresponding isocoumarin derivative, which is produced when concentrated sulphuric acid acts upon gallacetol, C₄H₃(OH)₃. CO.O.CH₂. COCH₃ (B. 26, 419).

Hydroisoquinolines.—1. Dihydroisoquinolines: a-Methyl Dihydroisoquinoline, C₄H₃(CH₃)N, boiling at 237-241°, and a-Phenyldihydroisoquinoline, C₅H₅(C₆H₅)N, molting at 195°, result when P₂O₅ or ZnCl₂ acts upon phenyl ethyl acetamide and phenethyl bensamide, C₅H₅CH₂. CH₃. NHCO. C₆H₅.

The n-alkyl derivatives of the isocarbostyrils are ketodihydroisoquinolines.

2. Tetrahydroisoquinolines: They are produced when isoquinoline is reduced with tin and hydrochloric acid, or, better, with sodium and alcohol. The pyridine nucleus is hydrogenized. Tetrahydroisoquinoline shows the properties of the alkylic benzylamines, while tetrahydroquinoline manifests those of an alkylic aniline:

while tetrahydroquinoline manifests those of an alkylic aniline:

Tetrahydrolsoquinoline, C_pH₁₁N, boiling at 233°, is a powerful base, which absorbs carbon dioxide from the air and reduces warm ammoniacal silver solutions. Its silverso-compound melts at 33°. The iodmethylate of n-methyl tetrahydroisoquino-line, C₂H₁₀N(CH₃)₂I, melting at 189°, is obtained from methyl iodide and tetrahydro-boquinoline. n-Benzoyl Tetrahydroisoquinoline, boiling at 245° to 250° (50 mm.), is converted by KMO₄ into ω-benzoylamidoethyl-o-benzoic acid,

C.H. COOH NHO NHCOC₆H₅ (p. 539). The latter readily parts with water and becomes the benzoyl derivative of-

Hydroisocarbostyril, Ketotetrahydroisoquinoline, C₆H₄<CO — NH, melting at 71° (B. 26, 1220).

The homophthalimides—e.g., $C_8H_4 < CO = NH$ (p. 244)—are diketotetrahydrolsoquinolines.

The alkaloids berberine, hydrastine, narcotine (p. 577), are derivatives of tetrahydroisoquinoline.

V. PHENANTHRIDINE.

It can be considered both as a benzo-derivative of quinoline and of isoquinoline. It results also from phenanthrene by replacing one of the intermediate — CH = groups by nitrogen:

It is isomeric with the naphthoquinolines (p. 553).

Phenanthridines are produced upon heating the acidyl derivatives of o-amidodiphenyl (B. 29, 1182):

$$\begin{matrix} C_{\bullet}H_{\bullet} & OCH \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

ORGANIC CHEMISTRY.

Phenanthridine, $C_{12}H_qN$, melting at 104° and boiling above 360°, results in the pyrogenic way from benzylidene aniline:

$$C_aH_bCH = NC_aH_b \xrightarrow{-2H} C_aH_4CH = NC_aH_4;$$

and when phenanthridone is distilled with zinc-dust. Bleaching lime and cobalt reoxidize it to phenanthridone (B. 26, 1964), while tin and hydrochloric acid reduce

it to dihydrophenanthridine, C₉H₄CH₅ — NHC₉H₄, melting at 90° (A. 256, 142).

ms-Methyl-, ethyl-, and phenyl-phenanthridine melt at 85°, 55°, and 109°
(B. 29, 1184).

Phenanthridone, C₈H₄CO. NHC₈H₄, melting at 293°, is produced on treating diphenamic acid with bromine and caustic potash:

$$C_{\mathfrak{g}}\Pi_{\mathfrak{q}} \longrightarrow C_{\mathfrak{g}}\Pi_{\mathfrak{q}} \longrightarrow C_{\mathfrak{g}}\Pi_{\mathfrak{q}} \longrightarrow C_{\mathfrak{g}}\Pi_{\mathfrak{q}} \longrightarrow C_{\mathfrak{g}}\Pi_{\mathfrak{q}} \longrightarrow C_{\mathfrak{g}}\Pi_{\mathfrak{q}}$$

as well as by the rearrangement of o-amidophenylene ketone (p. 418), on fusion with caustic potash; by transposition of diphenylene ketone oxime with zinc chloride, and, finally, from o-diphenyl urethane, $C_6H_6C_8H_4NHCO_2C_2H_6$, on digesting it with zinc chloride (B. 26, R. 712; 28, R. 455; 29, 230, 1188). Phenanthridone and phosphorus pentachloride

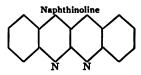
yield chlorphenanthridine, $C_6H_4CCl=NC_6H_4$, melting at 116°. n-Methyl Phenanthridone, $C_{13}H_3CNCH_3$, melting at 108°, is formed in the action of alkaline potassium ferricyanide upon methyl phenanthridinium iodide, $C_{13}H_9N$. ICH₃ (B. 26, 1962; compare pyridinium and quinolinium compounds, pp. 530, 544).

VI. NAPHTHYRIDINE, NAPHTHINOLINE.

The union of two pyridine nuclei or of two quinoline nuclei in the manner of naphthalene gives rise to the hypothetical parent substances:



and



Thus far only hydrides of these bodies have been prepared.

Octohydronaphthyridine, $C_n H_{14}N_2$ (forms a platinum salt), melts at 227°, and is prepared from γ_1 ; diamidodipropyl acetic acid (B. 26, 2137):

Tetrahydronaphthinoline, $C_{16}H_{14}N_2$, melting at 212°, is formed by the reduction of C_6H_4 — CH_2 —CH— CH_2 — C_6H_4 (p. 379), in a manner similar NO_2 OCOH NO_2 it to that of the naphthyridine body. Mercury acetate oxidizes it very easily to dikydro-the order of the naphthyridine body.

to that of the naphthyridine body. Mercury acetate oxidizes it very easily to dihydronaphthinoline, $C_{16}H_{12}N_2$, melting at 201°, the salts of which show an intense green fluorescence. It is reduced by sodium amalgam in glacial acetic acid solution to hexahydronaphthinoline, $C_{16}H_{16}N_2(+1\frac{1}{2}H_2O)$, melting at 128° (B. 27, 2244).

VII. ACRIDINE GROUP.

Acridine represents an anthracene, one of the intermediate CH-groups of which is replaced by nitrogen:

Its relations to quinoline and pyridine follow from its oxidation to quinoline dicarboxylic acid and pyridine tetracarboxylic acids (pp. 549, 538).

Acridine occurs in the crude anthracene of coal-tar. Different of its derivatives are important technically as dyes. Acridines may be synthesized:

1. From diphenylamine and acids, or from the acidyl derivatives of diphenylamine, if they be heated together with zinc chloride. This is analogous to the formation of the phenanthridines from acidyl-o-amidodiphenylenes (p. 557) (Bernthsen, A. 224, 1):

$$C_{\mathbf{e}}H_{\mathbf{5}} \xrightarrow{\mathbf{N}} C_{\mathbf{e}}H_{\mathbf{5}} \xrightarrow{\mathbf{C}} C_{\mathbf{e}}H_{\mathbf{4}} \xrightarrow{\mathbf{N}} C_{\mathbf{e}}H_{\mathbf{4}}$$

This reaction is a certain proof of the para-union in acridine.

Homologous acridines are similarly obtained from diphenylamine and the higher fatty acids. In them the hydrogen of the CH-group is replaced by alkyls. They are called meso-derivatives (B. 18, 690; 25, R. 940). The substituted diphenylamines (B. 24, 2039), ditolylamine, phenylnaphthylamine, etc., react just like diphenylamine.

2. Various acridine compounds have been prepared from the o-amido-derivatives of

di- and tri-phenylmethane (B. 26, 3085):

$$C_{6}H_{4} \xrightarrow{CH_{2}} C_{6}H_{5} \xrightarrow{C} C_{6}H_{4} \xrightarrow{C} C_{6}H_{4}$$
o-Amidodiohenvi Methane

Acridine.

3. Acridones are prepared from the alphylanthranilic acids (B. 26, R. 712; 27, R. 642), just as anthraquinone is obtained from benzoyl benzoic acid:

$$C_6H_6 \xrightarrow{HOCO} C_6H_4 \xrightarrow{CO} C_6H_4 < CO_{NH} > C_6H_4$$
Phenylanthranilic Acid Acridone,

or by the action of phenols (naphthols, etc.) upon acetanthranilic acid (B. 25, 1983, 2740).

The acridines are very stable compounds. They are more feeble bases than the pyridines and quinolines. They combine with alkyl iodides to alkyl acridinium iodides, which are converted by alkaline potassium ferricyanide (similar to the pyridinium and quinolinium iodides) into n-alkyl acridones. When the acridines are reduced they become dihydroacridines, which readily revert to the acridines.

Acridine, C₁₁H₂N, melts at 110°. It sublimes at 100°. Its solutions have a blue fluorescence. It is isomeric with phenanthridine and the naphthoquinolines. In addition to the general reactions it is also produced when diphenylamine is heated with chloroform and zinc chloride to 200° (B. 17, 101), and in the distillation of acridone with zinc-dust (B. 26, R. 714). Potassium permanganate oxidizes it to acridic acid, or quinoline-a, β-dicarboxylic acid, from which it was concluded that quinoline and pyridine had the diagonal formula (pp. 526, 541) (Riedel, B. 16, 1612).

In the oxidation of the acridinium compounds the heterocyclic nucleus is ruptured and

phenylamidobenzoic acid, C_6H_5 , NH. C_6H_4 , COOH, is produced.

ms-Methyl Acridine, $C_{13}H_8$ (CH₃)N, melting at 114°, is obtained from acetyldiphenylamine. Like quinaldine (p. 546) and picoline (p. 531) it combines with chloral to $C_{13}H_8$ NCH₂CH(OH)CCl₃. This is converted by alkalies into ms-acridyl-acrylic acid, $C_{13}H_8$ NCH: CH. COOH, which potassium permanganate oxidizes to acridyl aldehyde, $C_{13}H_8$ NCHO, and the latter to ms-acridyl carboxylic acid, $C_{13}H_8$ NCOOH (B. 20, 1541). 1541).

ms-Phenyl Acridine, C13H8(C8H5)N, results upon heating diphenylamine and benzoic acid. It crystallizes from benzene, with one molecule of benzene. It melts at 181°.

Chrysaniline, ms-p-Amidophenyl-2-amidoacridine,

C(C₆H₄NH₂) C₆H₄, melting at 268°, is the chief constituent of the beau tiful yellow dye, phosphin, which is obtained as a by-product in the rosaniline manufacture. It forms red colored salts; these dye silk and wool a beautiful yellow. Their

solutions exhibit a beautiful yellow-green fluorescence. The formation of chrysaniline from pararosaniline proceeds, evidently, according to

the diagram of method 2 for the acridines.

Dihydroacridine, C₆H₄< CH₂ > C₆H₄, is formed when acridine is reduced with zinc dust and hydrochloric acid. It no longer manifests basic properties, and melts at 168°. It reduces ammoniacal silver nitrate with the reformation of acridine.

Acridone, ketodihydroacridine, C₆H₄C₆H₄, melting at 354°, can be distilled. It is formed when sulphuric acid at 100° acts upon phenyl anthranilic acid, and by the dry distillation of the anilide of salicylic acid, when it may be assumed that the latter first rearranges itself to phenyl anthranilic acid. The salicyl toluides also yield methylated acridones (B. 29, 1189). PCl₅ converts it into chloracridine, C₆H₄< CCl N > C₆H₄.

melting at 119°. With methyl iodide and caustic potash it forms n-Methyl Acridone, C₆H₄CO - C₆H₄, melting at 203°, which is also produced when caustic potash and potassium ferricyanide act upon methyl acridinium iodide. Acridine is formed when acridone is heated with zinc-dust. Sodium and alcohol convert it into dihydroacridine. The following are obtained in the same way as acridone:

4-Methyl Acridone, CH₃.C₆H₃. (CO) NH C₆H₄, melting at 346°;

2 Methyl Acridone, melting at 338°; 2,4 Dimethyl Acridone, melting at 297° (B. 27, R. 642);

Phenonaphthacridone, C₆H₄< CO NII > C₁₀H₆; and

Dinaphthacridone, $C_{10}H_6 < {}_{NH}^{CO} > {}_{10}H_6$ (B. 25, 2744).

Peculiar acridine derivatives have been obtained by the condensation of acidyl carbazoles (B. 24, R. 829; 25, R. 114):

Benzoyl Carbazole ms-Phenylcarbazacridine, m. p. 186°.

Quinacridine,
$$C_6H_4 < \frac{CH}{N} > C_6H_3 < \frac{CH}{N} > C_6H_4$$
, melting at 213°, is a compound which was obtained in the zinc-distillation of an oxygen-containing body—oxyquinac-ridone. The latter results upon heating phloroglucin with anthranilic acid:

$$2C_6H_4 < \frac{COOH}{NH_2} + C_6H_6O_3 \longrightarrow C_6H_4 < \frac{CO}{NH} > C_6H(OII) < \frac{CO}{NH} > C_6H_4$$
It does not fuse. It begins to decompose above 400°. It is insoluble in almost all solvents. Sodium amalgam reduces quinacridine to tetrahydroquinacridine, melting at 272° (B. 29, 76).

$$2 C_e H_4 < _{NH_e}^{COOH} + C_e H_e O_s \xrightarrow{} C_e H_4 < _{NH}^{CO} > C_e H_{(OII)} < _{NH}^{CO} > C_e H_4.$$

VIII. ANTHRAPYRIDINES.

The a- and β -anthrapyridines are isomeric with acridine:

a-Anthrapyridine, C18 HoN, melting at 275°, results from the reduction of a-anthrapyridine quinone, C₀H₄< $\stackrel{\text{CO}}{\text{CO}}$ >C₅H₃N, melting at 280°, which is made by condensing β -benzoyl picolinic acid with sulphuric acid. β -Anthrapyridine, melting at 166°, is similarly formed from β -anthrapyridine quinone, the condensation product of γ -bensoyl nicotinic acid (B. 28, 1658).

ALKALOIDS.*

Formerly, all nitrogen-containing bodies occurring in plants, and possessing basic, alkaline character, or derivatives of the same, from which bases could be isolated, were designated as alkaloids.

Many of them (betaine, asparagine, theine; 1, 310, 490, 515) have, in accord with their constitution, been already discussed with the various amido-derivatives; the most of those remaining which have been studied recently show themselves to be derivatives of pyridine, quinoline, and isoquinoline, or of their corresponding hydro-derivatives. Several have been prepared artificially (piperine, conine, trigonelline, and arekaidine); in the case of others, synthesis has had the way made plain by analysis, or it has been attained, as in the case of hydrastine, for the basic decomposition product of the alkaloid. Like the benzene derivatives, they have much in common in their whole deportment. They are the chief

^{*}Consult "La Constitution chimique des Alcaloïdes végétaux," par Amé Pictet. Paris, G. Masson, 1897 (II. ed.).

constituents of the active principles of the vegetable drugs employed as medicines or poisons.

Because of their great number and their ofttimes unusually remarkable physiological and pharmacological properties they constitute one of the most interesting classes of carbon compounds.

Occurrence.—The vegetable alkaloids occur almost exclusively in the dicotyledons; but one, the poorly investigated colchicine, is formed in a monocotyledon, while the large families of the Composite and Labiate do not furnish them. In plants they are generally combined with widely distributed plant acids—e.g., malic acid (1, 487), citric aid (1, 529), and tannic acid (p. 543). Many are accompanied by acids which usually are found associated with definite alkaloids—e.g., the opium alkaloids are united with meconic acid (p. 523), and the quinia alkaloids with quinic acid (p. 301). The alkaloids prized for their pharmacological properties are the subject of technical isolation. The artificially prepared carbon compounds, having similar physiological action, hold a subordinate position compared with them—e.g., quinine and antipyrine (p. 488); atropine and several tropelnes (p. 567); cocalne and eucaine (p. 540).

Some alkaloids contain no oxygen, and then are generally liquid and volatile—e. g., piperidine, conine, nicotine, and sparteine. Most of them do, however, contain that element, and are solid and non-volatile. Nearly all are tertiary amines; some, however (like the hydrides of the pyridine nucleus, belong to the secondary amines. Many (like pilocarpine) are ammonium bases. Tannic acid, phospho-molybdic acid, platinic chloride, and many double salts (like HgI₂. KI) precipitate all these bases from their aqueous solutions. The bases are regained from these compounds by alkalies.

The alkaloids have a more or less bitter taste. Most of them are optically active and, indeed, lævorotatory (1, 67). Conine, naratine, and pilocarpine are dextrogyratory. Piperine is inactive. Many alkaloids give characteristic colors with chlorine water, nitric acid, or concentrated sulphuric acid.

I. THE PYRIDINE GROUP OF THE ALKALOIDS.

Piperine, C₁₇II₁₉NO₂=CII₂ CH₂-CH₂ N.CO.CH:CH.CH:CH[I]C₆H₃ {[3]O CH₁ melting at 128°, occurs in different varieties of pepper, the fruit of *Piper nigrum* and *Piper longum*. It dissolves with a deep red color in sulphuric acid. It is decomposed by Indian algorithms also be a large red color of the property of the p

by boiling alcohol into piperidine and piperic acid.

The two decomposition products of piperine have been built up from their elements, and by allowing the chloride of piperic acid to act upon piperidine the synthesis of piperine itself has been realized (B. 27, 2958). The synthesis of conine presupposes that of piperidine, and is represented by diagram under conine. Artificial piperines have been prepared from the synthetic a-alkyl and a-phenyl piperic acids with the assistance of the chlorides (B. 28, 1195).

a-Conine, d,a,n-propyl piperidine, $C_8H_{11}N=CH_2$ CH₂—CH₂—CH₃. CH₄. CH₄. CH₅

boiling at 167°, with sp. gr. 0.886 (0°), $[a]_D=+$ 18.3 (B. 27, 3062), occurs together with n-methyl conine and γ -coniceine, $CII_2 < CII_2 - C(C_3H_2)$ NH (B. 28, 302), conhydrin, and pseudoconhydrin

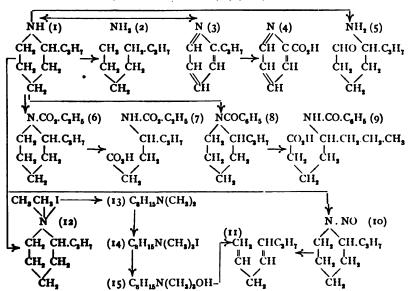
(p. 564), in hemlock (Conium maculatum), especially in the seeds. a colorless liquid with a stupefying odor. It is a very powerful poison.

History: Giesecke (1827) discovered conine. A. W. Hofmann (1881) determined its molecular magnitude, and in 1884 demonstrated that it yielded conyrine or a-propyl pyridine upon distillation with zinc-dust. Obtaining picolinic acid by oxidation, he thus proved the a-position of the propyl group. The synthesis of optically inactive conine, its decomposition into d- and 1-conine, and thereby the first complete synthesis of an optically active alkaloid, are due to Ladenburg (1886) (B. 22, 1403).

The following diagrams represent the decomposition of conine, which corresponds to that of piperidine (p. 539), and also the synthesis which presupposes that of piperi-

dine and pyridine.

Decomposition of Conine: The reduction of natural d-conine (1) by hydriodic d resolves it into n-octane (2) and ammonia (B. 18, 13). The distillation with zincacid resolves it into n-octane (2) and ammonia (B. 18, 13). The distillation with zinc-dust leads to convrine (3), or a,n-propyl pyridine, which hydriodic acid reduces to inactive [d+1]-conine, while upon oxidation it becomes picolinic acid (4) or pyridines-carboxylic acid. Hydrogen peroxide oxidizes conine to δ-amido-n-octyl aldehyde, or δ-propylamidovaleraldehyde (5) (B. 28, 1460). Nitric acid oxidizes conylurethane (6) to carbethoxyconinic acid or y-carboethylamido-n-heptan acid (7) (B. 15, 1947), which Potassium permanganate yields coninic acid when heated with hydrochloric acid. oxidizes benzoyl conine to benzoyl homoconinic acid or δ-benzoylamido-n-octan acid (8) and benzoyl-a-amidovaleric acid (9) (B. 19, 502). Nitrous acid converts conine into nitroso-conine (10), which breaks down, on heating with phosphorus pentoxide, into water, nitrogen, and convlene (11). Methyl iodide and conine combine to dimethylconinium iodide (12), which is changed by sodium hydroxide to dimethylconine, C₈II₁₅N(CH₃)₂ (13) (B. 14, 708), of uncertain constitution (A. 279, 341). Dimethyl conine and methyl iodide also combine, and the resulting iodide (14) is converted by silver oxide into trimethyl conylium hydroxide, $C_8H_{18}N(CH_3)_3OH$ (15), which breaks down, upon distillation with water, into trimethylamine and convlene (10) (1, 99):



Synthesis of Conine (B. 22, 1404). We begin with the synthesis of trichloracetic acid (1, 274), which by reduction yields synthetic acetic acid (1, 244). From this we proceed to glycerol (1, 471), which can be converted into allyl bromide. Allyl bromide and hydrobromic acid combine to trimethylene bromide, the latter yielding, by the action of trimethylene cyanide, pentamethylene diamine, from which piperidine results by the elimination of ammonia (1, 314). Piperidine may be oxidized to pyridine, the iod-methylate of which—pyridinium iodide—is changed at 300° into a-picoline iodhydrate. Picoline and parallehyde at elevated temperatures yield a-allyl pyridine, which is reduced to inactive conine.

d-Conine d-tartrate separates first from a solution of dextro-tartrate of inactive conine; and caustic potash resolves it into a conine identical with the natural conine. As dextro-tartaric acid can be prepared from synthetic racemic acid (1, 523) the synthesis of conine is complete.

d-Conine Hydrochloride melts at 218°. Nitroso-d-conine is a bright yellow-colored oil. d-Conylene Urethane boils at 245°. Benzoyl-d-conine is a thick oil.

Inactive r- (racemic) or (d + 1)-conine and 1-conine behave physiologically and chemically like d-conine. Sodium and alcohol also reduce a ethyl pyridyl ketone to (d + 1)-conine. The first product is a-ethyl pyridine alkine, a-ethyl pyridyl carhinol, boiling at 213-218° (p. 535), then a-ethyl piperyl alkine, C₂H₂NHCH(OH). CH₂. CH₃, melting at 100°, identical with pseudoconhydrine, which has also been discovered in Conium maculatum. Inactive conine is best prepared by reducing y-coniceline (p. 538) (B. 29, 1956).

Isoconine or Isoconicine—consult B. 27, R. 203; 29, 1959, 2706 (see 1, 511).

haso, occurs in the seeds of *Trigonella fanum gracum*, and in small amount, together theolise, in the seeds of *Pisum sativum*, and also in flax—*Cannabis sativa*. As Jahns shown, trigonelline is identical with nicotinic acid betaine, synthesized by Hantzsch (B. 27, 769).

Arecaldine, Tetrahydronicotinic Acid Methyl Betaine, $C_5H_8(COO)\dot{N}$. CH₃ ($+H_2O$), taking at 224°, occurs, together with arecoline, $C_8H_{13}NO_3$ (chief constituent), arecaine, $C_8H_{13}NO_3$, and guvacine, $C_8H_3NO_3$, in the nut of Areca Catechu. It and its dihydronicotinic acid methyl betaine, have been obtained with the chlormethylate of nicotinic ester by the action of tin and hydronicotic acid. It forms arecoline, boiling at 209°, when treated with methyl alcohol and the constitution of the property of the constitution of arecalment and the constitution of arecalment and guvacine has not yet been definitely established.

Pilocarpine, CH
$$CH = CH$$
 N CH_{0} CH_{0}

pidine, CH
$$CH = CH$$
 N $C < CH_3$ CH_3 , occur in the Jaborandi leaves of *Pilocarpus* $COOH$

pennatifolius.

Pilocarpine is a poison which acts like nicotine (A. 238, 230). The injection of it into milch cows occasions a very appreciable increase in the sugar of the milk (B. 26, R. 247). When pilocarpine is treated with hydrochloric acid, or when it is boiled with water, it changes in part to pilocarpidine, and in part to β-pyridine-α-lactic acid (p. 538) and trimethylamine. Potassium permanganate oxidizes pilocarpine nitrate to β-pyridine tartronic acid, which by further oxidation becomes nicotinic acid. β-Pyridine-α-lactic acid and PBr₃ form β-pyridine-α-brompropionic acid, which trimethylamine converts at 150° into pilocarpidine. By treating pilocarpidine with methyl iodide and caustic potash, then oxidizing the methyl group, which has attached itself to the pyridine nitrogen, with silver permanganate, pilocarpine is produced (Hardy and Calmels, B. 19, R. 703; 20, R. 575; see B. 28, 1762).

Cytisine, Ulexine, Sophorine, C₁₁H₁₄N₂O, melting at 152°, occurs in the seeds of Cytisus Laburnum, as well as in other Cytisus-varieties, in Ulex europeaus and in Sophora tomentosa and speciosa (B. 23, 3201; 24, 634; 27, R. 509, 884; 28, R. 237; 29, R. 36, 53).

Nicotine, a Pyridyl-β-tetrahydro-n-methyl pyrrol (?),

$$C_{10}H_{14}N_{2} = \begin{bmatrix} C_{11} & N_{12} & C_{13} & C_{14} & C_{14}$$

lævogyratory (B. 26, R. 193), occurs in the leaves of the tobacco plant, *Nicotiana tabacum*, in quantities varying from 0.6 to 8 per cent., depending upon the varieties. As a rule, the better qualities of tobacco contain less nicotine than the poorer sorts.

Nicotine is very soluble in water. It has a disagreeable odor and burning taste. It is a very violent poison.

Potassium ferricyanide, or, better, silver oxide, oxidizes nicotine (1) to nicotyrine (2) or a- β -pyridylmethyl pyrrol (?) (B. 27, 2535). Nitric acid, chromic acid, or potassium permanganate oxidize it to nicotinic acid (3) or β -pyridine carboxylic acid (A. 196, 130; see also B. 30, 2122), while with hydrogen peroxide it yields oxynicotine, $C_{nl}l_{nl}$. N_s(0) (B. 28, 456). Sodium and alcohol reduce it to hexahydronicotine (4) (B. 26, 765). With bromine and water nicotine forms dibromnicotine (5) $C_{10}H_{n}Br_{n}N_{n}O_{2}$, which barytawater resolves into methylamine, malonic acid (6), and nicotinic acid (B. 26, 292). Nicotine takes up benzoyl chloride, with rupture, very probably, of the pyrrolidine ring. Hydrochloric acid liberates nicotine from the addition-product, while sodium alcoholate produces a secondary base, metanicotine, isomeric with nicotine and melting at 275-278°. It is probably ω -methylamido-propylidene- β -picoline.

History: Posselt and Reiman discovered nicotine (1828). Since 1891 Blau, but more especially Pinner, has studied its transposition reactions. The constitutional formula proposed by Pinner harmonizes with its deportment, and has more recently been fortified by the experiments of Amé Pictet and Crépieux (1895), which doubtless will eventually terminate in a synthesis of nicotine.

Pictet and Crépieux let potassium hypobromite act upon nicotinamide (8) and obtained β -amidopyridine (9), which (p. 458) becomes N, β -pyridyl pyrrol (10) upon distillation with nucle acid. If N, β -pyridyl pyrrol be conducted through tubes heated to faint redness, it is rearranged to a,β -pyridyl pyrrol (11), which methyl iodide converts very probably into nicotyrine iodimethylate (12) (B. 28, 1909).

The preceding diagram represents a tabular view of the rearrangement reactions of

ecotine and the production of nicotyrine iodmethylate from nicotinic acid.

Sparteine, Cl_BH₂₆N₂, boiling at 311°, is a colorless, thick oil, occurring in *Spartium* **spartium**. It is a diacid base and is a powerful narcotic. Tin and hydrochloric acid induce it to dihydrosparteine, Cl_BH₂₆N₂, while hydrogen peroxide oxidizes it to mono-, F-, and trioxysparteine (B. 30, 195). Hydriodic acid splits off a methyl group from narteine (B. 21, 826). Diethylmethylamine, pyridine, and α-picoline are produced then it is distilled with zinc-dust (B. 26, 3035).

II. TROPINE GROUP.

Solanum Bases.—Several very similar alkaloids are found in many arieties of solanum, of which the best known are the two isomerides: opically inactive atropine, discovered by Mein in 1833, as well as by Geiger and Hesse, and lævogyratory hyoscyamine. If they are introduced in very mall quantity into the eye they cause dilatation of the pupil, and are herefore used in medicine as mydriatics. Both bases are found in Tyoscyamus niger and albus, in Datura stramonium, in the deadly nighthade, Atropa belladonna, and in Dubotsia myoporoides. The less invesigated bases which accompany them are belladonine (B. 17, 152, 383), poscine, scopolamine (B. 25, 260; 29, 1771, 2009, 2439), apoatropine below) (B. 25, R. 573; 26, R. 285), all of which, as acid decomposition products, yield tropic and atropic acids; as basic constituents they ield bodies closely allied to tropine.

hanges in part to atropine on treatment with aqueous or alcoholic odium hydroxide (B. 21, 1717, 2777, 3069). It is very probable that the wo bases are physical isomerides. Atropine is decomposed into tropine acid, or a-phenylhydracrylic acid, $CH_2OH \cdot CH(C_6H_5)CO_2H$ p. 252), when it is heated with hydrochloric acid or baryta-water. Conversely, atropine is formed when tropic acid and tropine are evaporated with dilute hydrochloric acid (Ladenburg).

Both the basic and the acid decomposition products of atropine contain symmetric carbon. Indeed, tropic acid has been resolved into its opically active components, and from tropine there have been obtained with dextro- and lævo-tropic acid: dextro-atropine, melting at 110° to 120°, and lævo-atropine (B. 22, 2590). The latter is very similar to lævo-ayoscyamine, but it is not identical with it.

Apoatropine, Atropamine, $C_{17}H_{21}NO_{2}$, melting at 60-62°, results from the action of aitric acid upon atropine. It is made synthetically by evaporating tropine atropate with lilute hydrochloric acid. It is decomposed by baryta-water into tropine and atropic acid [p. 278]; it is the tropelne of atropic or a-phenylacrylic acid.

Tropelnes.—Just as tropine yields atropine with atropic acid, so it is capable of entering combination with other acids producing ester-like derivatives, which have been called tropelnes (Ladenburg, A. 217, 82; 27, R. 202). Of these, phenylglycolyl-tropelne, or Homatropine, C_gH₁N(CH₃). C₂H₄. O. CO. CH(OH). C₆H₅, is noteworthy because its mydriatic action is not so prolonged. It is obtained from tropine and mandelic

acid. It is employed as a substitute for atropine, and is applied in the form of hydrobromide. It melts at 95.5-98.5°.

Only those tropelnes possess mydriatic action in which the acid radical contains also-holic hydroxyl.

Lactyl Tropeine melts at 74° (B. 28, R. 492).

Benzilo-tropeine is the tropeine of benzilic acid (p. 367) (B. 27, R. 202).

Tropine, CH-CH₁-CH(OH) CH, melting at 62° and boiling at 233°, is the basic CH₂-N(CH₃)

decomposition product of atropine. Merling regards it as an n-methyl piperidine, the and β -carbon atoms of which are joined through the group — CH_2 — CH(OH) —, so that tropine can, upon the other hand, be viewed as an oxyhexahydrobenzene derivative. Ecgonine, the basic decomposition product of cocalne, is a tropine carboxylic acid. These kinships will in a measure account for the similar actions of atropine and cocalne. As ecgonine is not capable of forming a lactone, Einhorn assumes that its alcoholic hydroxyl is attached to the β -carbon atom, and this explains the formula given above for tropine.

The constitution of tropine follows further from its decomposition reactions. We are indebted mainly to Ladenburg and Merling for our knowledge of these:

Decomposition of Tropine.—a. Conversion of tropine into tropic acid, and into active pyridine and picolinic acid: Potassium permanganate oxidizes tropine (1) to tropigenine (2), whereas with chromic acid it first yields a ketone, tropinone (3), which upon reduction does not yield tropine again, but a \$\psi\$-tropine, which is always obtained by the decomposition of an alkaloid associated with cocaine (p. 569) (B. 29, 1636, 2228). When tropinone is further oxidized with chromic acid, tropic acid (4) results, which by proper decomposition is converted into normal adipic acid (B. 28, 3271). Glacial acetic acid and hydrochloric acid split off water from tropine, and tropidine (5) results. The latter is oxidized by potassium permanganate to dihydroxytropidine (6). Further oxidation changes this body to tropic acid (4) (B. 28, 2277). Zinc and hydrochloric acid reduce tropidine to hydrotropidine (7), a saturated compound, the chlorhydrate of which splis off methyl chloride in a current of hydrochloric acid gas, and becomes nordihydrotropidine (8). When the latter is distilled with zinc-dust, a-ethyl pyridine (9) is produced, which upon oxidation becomes picolinic acid (Ladenburg, B. 20, 1647):

b. The conversion of tropidine into benzyl bromide (Merling, B. 24, 3108; 26, 1060). Tropidine (1) takes up methyl iodide, and, exposed to moist silver oxide, exchanges the iodine atom for hydroxyl, with the formation of tropidine methyl ammonium hydroxide (2), which is converted by boiling water into a-methyl tropidine or Δ₂₁₅-dihydrobenzyldimethylamine (3). a-Methyl tropidine adds methyl iodide and acts further like the preceding body, with the production of a-methyl tropidine methyl ammonium hydroxide (4), which boiling water changes to tropilidene (5). The latter takes up two bromine atoms: its dibromide (6), heated to 100°, breaks down into HBr and benzyl bromide (7). Einhorn and Willstätter (A. 280, 96) view tropilidene as a dihydrobenzene, in which two C-atoms holding the p-position are linked by the CH₂-group, similar to what we have, according to Bredt, in camphor. Consult B. 29, 402, 490; 30, 721, for analogous decompositions of tropinone and dihydrotropidine.

Synthesis of Tropine.—a-Methyl tropidine or $\Delta_{2,5}$ -dihydrobenzyldimethylamine (1) forms a dihydrochloride: hydrochlor-a-methyl tropidine chlorhydrate (2). Sodium hydroxide splits off hydrochloric acid from this and there remains tropidine methyl ammonium chloride (3). By distillation the latter changes to tropidine (4), which takes up water on boiling with caustic alkali and reverts to tropine :

tory. It is present in the leaves of Erythroxylon coca. It is a very superior local anæsthetic, and is applied in the form of hydrochloride. When it is digested with hydrochloric acid it breaks down into ecgonine, benzoic acid, and methyl alcohol.

It yields benzoyl ecgonine and methyl alcohol when boiled with water.

Conversely, cocaine can be again re-formed from ecgonine, from benzoyl ecgonine, and from benzoyl ecgonine ester by introducing benzoyl into ecgonine ester, or, better, by esterifying benzoyl ecgonine with methyl alcohol. In this way certain alkaloids—e. g., cinnamyl cocaine, truxilline, etc.—associated with cocaine (B. 27, 783 Anm.) become valuable technically. In their decomposition they yield ecgonine methyl ester and ecgonine

(B. 22, 2960, R. 953).

Truxillic Acids, C_6H_5 . CH - CH. CO_2H C_6H_5 . $CH - CH - CO_2H$ Collinamic acids, dicinnamic acids, and also "natural isocinnamic acid," were discovered by Liebermann in his study of the secondary alkaloids of cocaine. By distillation they yield ordinary cinnamic acid. The a-acid melts at 274° ; the β -acid at 206° .

Acetic anhydrida and sedium acetate convert the first jute the aphydrida (m. p. 101°) Acetic anhydride and sodium acetate convert the first into the anhydride (m. p. 191°) of y-truxillic acid, melting at 228° (B. 22, 126). When the β -acid is fused with caustic potash it changes to δ -truxillic acid, melting at 174°. Potassium permanganate oxidizes the \(\beta\)-acid to benzil (B. 22, 2254)—a reaction which, together with the inability to take up bromine and the stability of β -truxillic acid toward cold potassium permanganate, argues for the constitutional formula given above (B. 27, 1410).

d-Cocaine, melting at 43-45°, occurs in small quantities in the mixed cocaine bases (B. 23, 926). It is obtained synthetically from d-ecgonine (B. 23, 982). See B. 27,

1874, 1880, for cocaines substituted in the benzoyl group.

Tropa-cocaine, Benzoyl-\(\psi\)-tropine, \(C_{15}H_{19}NO_2\), melting at 49°, and found in

small amounts in the coca alkaloids, breaks down into benzoic acid and \$\psi\$-tropine, melting at 108° and boiling at 241°. The latter appears to be a stereoisomeride of tropine, because it can also be prepared by the reduction of tropinone, and when oxidized revers to the latter. Indeed, tropine can be directly rearranged to \$\psi\$-tropine by means of sodium amylate. Potassium permanganate oxidizes \$\psi\$-tropine to \$\psi\$-tropine, which, like tropigenine, yields nortropinone upon oxidation (B. 29, 936, 1636, 2231).

Mention may also be made here that crude cocalne contains small quantities of Hygrine, C₈II₁₅NO, boiling at 92-94° (20 mm.). It is a derivative of n-methyl pyrolipide (COCH₂CH₃)

dine, probably CII-CH > NCH₃, as it forms an oxime, and when oxidized becomes hygric acid, or methyl pyrrolidine carboxylic acid, which parts with carbon dioxide very readily (B. 28, 578) (p. 461).

at 205° when anhydrous. It is the basic decomposition product of 1-cocaine. When digested with caustic potash it changes to d-ecgonine, melting at 254°. See B. 24,7; 26, 962, for tife esters, amides, and nitriles of the ecgonines.

a-Ecgonine, CH CII₂—C(OH) CH , melting at 305°, is a position isomeride CII₂—N(CII₃)

of ecgonine. It has been prepared by adding hydrocyanic acid to tropinone (p. 568) and then saponifying the cyanhydrin (B. 29, 2216).

Anhydroecgonine (see below), melting at 234°, is produced on boiling ecgonine hydrochloride with phosphorus oxychloride (B. 20, 1221). The connection or relation of ecgonine to tropine follows as a consequence of the rearrangement of anhydroecgonine (observed by Einhorn), upon heating with hydrochloric acid to 280°, into tropidine, carbon dioxide being eliminated (B. 23, 1338).

Decomposition of Ecgonine: The conversion of anhydroecgonine into p-toluic

Decomposition of Ecgonine: The conversion of anhydroecgonine into p-toluic acid and terephthalic acid gives a clue as to the position of the carboxyl group in the tropidine ring of anhydroecgonine and also in ecgonine (B. 27, 2439). If the anhydroecgonine (2) obtained by treating ecgonine hydrochloride (1) with POCl₂ be acted upon with methyl iodide after its conversion into the ethyl ester, anhydroecgonine ethyl ester iodimethylate (3) will be produced, and moist silver oxide will change it to anhydroecgonine methyl betafine (4). Boiling alkalies convert the latter into dimethylamine and p-methylene dihydrobenzoic acid (5), melting at 33°. Its amide melts at 125°. By the addition of 211Br p-methylene dihydrobenzoic acid becomes p-toluic acid dihydrobromide (6), which boiling sodium hydroxide changes to p-toluic acid (7), and terephthalic acid (8) is its oxidation product. The reduction of p-methylene benzoic acid produces $\Gamma a \Delta_2$ -4-ethylcyclopentene Carboxylic Acid (9), boiling at 250-253°. Its amide melts at 158°.

$$(1) \begin{array}{c} \operatorname{CH}_2 - \operatorname{CH}_2 \\ \operatorname{CH}_3 - \operatorname{CH}_3 \\ \operatorname{CH}_3 - \operatorname{CH}$$

If the preceding formula is correct, then p-methylene dihydrobenzoic acid would have as basis a ring-system similar to that observed with camphor (A. 280, 96; B. 27, 2439). Hydroecgonidine, C₂H₁₈NO₂, melting at 200°, is a saturated body. It is formed in the adaction of anhydroecgonine, and it can be decomposed like the latter. Here, however, the intermediate product, lacking above, between (4) and (5) can be fixed. It is a stranhydrodimethylbenzylamine-p-carboxylic ester, the iodmethylate of which rieds tetrahydromethylene benzoic acid when decomposed with alkali (B. 30, 702).

fields tetrahydromethylene benzoic acid when decomposed with alkali (B. 30, 702).

Pelletierine, C,H_{II}NO, iso-, methyl-, and pseudopelletierine (named after the themist Pelletier), was discovered by Tauret in *Punica granatum*. Pseudopelletierine alone has been closely studied by Ciamician and Silber. They recognized this base as a

near relative of the tropine series.

Pseudopelletierine, C₅H₁₅NO (2), melting at 48° and boiling at 246°, corresponds to ropinone (p. 568). By reduction it yields the alcohol corresponding to tropine: methyl granatoline (1), which chromic acid again converts into pseudopelletierine and subsequently oxidizes to methyl granatic acid (3), corresponding to tropic acid, whereas potassium permanganate splits off the methyl group and forms granatoline, pologous to ropigenine (p. 568). Hydriodic acid and phosphorus reduce methyl granatine (4) and granatine (5); the latter, distilled with zinc-dust, yields a-propyl pyriatine (6):

When pseudopelletierine is decomposed with methyl iodide and alkali it is changed into a dihydroacetophenone analogous to dihydrobenzaldehyde. It, therefore, conducts itself like a ring homologue of tropinone (B. 29, 481, 2972).

III. QUINOLINE GROUP OF THE ALKALOIDS.

Quina-bases.—The quina-barks (cortex chinæ) are derived chiefly from the various Cinchona species: Cinchona Calisaya, C. lancifolia, C. Pitayensis, etc.; also from the Rubiaceæ. They contain, in addition to tannin and quinic acid (p. 301), a series of bases, the most important of which are:

Quinine, CH₃O. C₅H₅N. C₅H₁₁(OH)(CH₃)N (?) + 3H₂O, melts, when anhydrous, at 177°. It consists of silky needles when crystallized from alcohol and ether. Pelletier and Caventou discovered quinine in 1820. It is one of our most valued medicines, especially for intermittent fevers, —e. g., malaria, etc.,—and is an antidote for many infections produced by micro-organisms.*

^{# &}quot; Grundzüge der Arzneimittellehre," von C. Binz, 12. Aufl., 1894.

It is found (2-3 per cent.) in the yellow calisaya bark. It reacts alkaline, tastes bitter, and being a diacid base, forms primary and secondary salts.

The neutral sulphate, $(C_{30}H_{24}N_2O_2)H_2SO_4+8H_2O$, and the primary hydrochloride, $C_{30}H_{24}N_2O_2$. $HCl+2H_2O$, are employed in medicine. The former consists of long, shining needles, which fall to a white powder on exposure. It dissolves readily in dilute sulphuric acid, the solution exhibiting a beautiful blue fluorescence.

When chlorine water and then ammonia are added to the solution of quisine salt, there is produced a green precipitate, dissolving in an excess of ammonium hydroxide with an emerald-green color. On adding an alcoholic iodine solution to the sulphate in acetic acid, a periodide, 4Qu. 3SO₄H₂. 2HI. I₄ + 6H₂O, called herapathite, is precipitated. This crystallizes in emerald-green plates with golden lustre, and polarizes light the same as tourmaline.

Quinine is a tertiary diamine, and with metallic iodides yields the iodides, C₂₀H₂₄N₂O₂. CH₃I and C₂₀H₂₆N₂O₃. 2CH₃I. The first of these yields the so-called methyl quinine, C₂₀H₂₂(CH₃)N₂O₃, when it is boiled with caustic potash. See B. 26, 1968, for the ethyl iodide derivatives.

Cinchonine, C₉H₆N. C₉H₁₁(OH)(CH₂)N, is associated with quinine and occurs principally in the gray quinia bark (*Cinchona Huanaco*) (upward of 2.5 per cent.). It crystallizes from alcohol in white prisms, sublimes in needles in a current of hydrogen, and melts at 255°. Like quinine, it seems to dissipate fever, but to a less degree. Cinchonine is converted by boiling amyl alcoholic potash into cinchonidine (m. p. 201°), which is probably a stereoisomeride (B. 29, 2185).

Quinine and cinchonine are similarly constructed; they contain one hydroxyl, and the former an additional methoxyl group. It is, therefore, methoxycinchonine:

$$C_{19}H_{21}(OH)N_3$$
 $C_{19}H_{20}(O.CH_3)(OH)N_2$ Cinchonine Quinine.

They yield acetyl derivatives when heated with acetic anhydride. Quinine heated to 150° with hydrochloric acid splits off the methyl group, with formation of apoquinine, C₁₉II₂₀(OH)₂N₂. The two nitrogen atoms of both alkaloids are tertiary.

Decomposition of Cinchonine and Quinine: When cinchonine (1) and quinine are boiled with acetic acid, the union of that carbon atom to which hydroxyl is attached is severed from the one nitrogen atom, which then becomes an imido-group, while the C(OH)-group becomes a keto-group. Cinchonine yields the isomeric quinchotoxine (2), melting at 58-60°, which, like the corresponding quinotoxine, is very poisonous, but does not have any antipyretic properties. Quinchotoxine forms a methyl derivative (4), the iod-methylate of which appears to be identical with that of methyl cinchonine. The latter has been prepared by adding methyl iodide to cinchonine (3) and splitting off hydriodic acid (B. 13, 2292).

These observations have led v. Miller and Rhode (B. 28, 1056) to regard cinchonine, which contains a quinoline ring, as a compound of quinoline with a piperidine ring, effected through a CH₂-group. The N-atom of the piperidine ring is linked through the group C(OH), to which the CH₂-group is attached, with the γ -carbon atom of the piperidine ring. The formulas recall those of tropine and ecgonine (p. 568):

(3)
$$CH = CH_2$$
 (4) $CH = CH_2$

$$CH \xrightarrow{CH_2 - CH_2} N(ICH_3) \longrightarrow CH \xrightarrow{CH_2 - CH_2} N(CH_2)$$

$$CH_2 - C(OH) \xrightarrow{CH_2 - CH_2} N(CH_3)$$

$$CH_2 - CO \longrightarrow CH_2 \cdot C_9H_6N.$$

The following of the many other decomposition reactions of cinchonine and quinine may be considered:

Oxidation of Cinchonine and Quinine: Potassium permanganate oxidizes cinchonine to cinchotenine, $C_{12}H_{20}N_2O_3 + 3H_2O$, melting at 197°. This is an oxycarboxylic acid, which can be as readily decomposed into a keton-imide as cinchonine itself. When cinchotenine is formed, formic acid appears, and a vinyl group probably becomes a carboxyl group. This would seem to be indicated by the addition of two bromine atoms, one molecule of hydrogen chloride, or H1 to cinchonine (B. 19, 2856). Cinchonine and quinine, when more energetically oxidized with potassium permanganate, yield cinchoninic acid, quinic acid, and eventually $a_1\beta_1$ -pyridine tricarboxylic acid, or carbocinchomeronic acid (p. 536). It follows from this that cinchonine and quinone are y-quinoline derivatives. When oxidized with chromic acid and dilute sulphuric acid, cinchonine (1) and cinchotenine yield, in addition to cinchoninic acid (3), cincholoponic acid (5) ($\lambda ox \phi_5$, "remaining"), $C_0H_{13}NO_4 + H_2O$, melting at 125-127° with decomposition. This is probably a hexabydrohomocinchomeronic acid, $C_5H_5N(CH_2COOH)(COOH)$ (B. 28, 12; 29, R. 843; 30, 1326). Cincholoiponic acid (5) is also found, when chromic acid, which is a methoxy-y-quinoline carboxylic acid (4).

$$C_9H_6N.C_{10}H_{15}(OH)N \longrightarrow \begin{cases} \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \\ \end{array} \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \\ \\ \end{array} \\ \\ \\ \\ \\$$

On the other hand, cinchonine is broken down by a chromic acid mixture into cinchoninic acid and meroquinene (from $\mu i \rho \rho c_s$, "part"). The latter also results from a hydrolytic decomposition of cinquene and quinene, brought about by phosphoric acid at 170-180°. Lepidine or y-methyl quinoline and p-methoxylepidine are produced at the same time. Meroquinene is converted into β -thyl-y-middine on heating with corrosive sublimate and hydrochloric acid. When oxidized it becomes cincholoiponic acid. It probably should be regarded as β -vinyl-y-piperidine acetic acid (B. 30, 1326).

acid. It probably should be regarded as β -vinyl- γ -piperidine acetic acid (B. 30, 1326). Lepidine and methoxylepidine are also formed in the alkali fusion of cinchonine and

quinine (B. 23, 2675).

Decomposition of Cinchonine and Quinine Chlorides: PCl₅ converts cinchonine and quinine into cinchonine and quinine chlorides, and these compounds, boiled with alcoholic potash, yield cinchone and quinene, which, when heated to 190° together with concentrated hydrochloric or hydrobromic acid, give up ammonia and absorb water, thus forming apocinchene and apoquinene:

When apoquinene is heated to 250° with zinc ammonium chloride it becomes amido-apocinchene, from which apocinchene may be obtained through the diazo-compound. As cinchonidine and conquinine can also be changed to cinchene and quinine, the four quinia-alkaloids (Königs, B. 27, 903), cinchonine, quinine, cinchonidine, and conqui-

nine, are derived from cinchene. On the other hand, when the chlorides of the four alkaloids are reduced and the chlorine atoms replaced by hydrogen, four different desoxycompounds result: desoxycinchonine, desoxycinchonidine, desoxyquinine, and desoxycompounds. The isomerism of the two pairs of alkaloids appears, therefore, to be occasioned by the asymmetry of the tertiary carbon atom to which hydroxyl is attached.

Decomposition of Apocinchene into γ-o-Oxyphenyl Quinoline: Apocinchene is a phenol. Its ethyl ether (1) can be gradually oxidized to ethyl apocinchenic acid (2), the lactone of ethyl apocinchene oxy-acid (3), and quinoline phenetol-dicarboxylic acid (4), which forms an inner anhydride very readily, and consequently contains the CO₂H-groups in the o-position. Boiling concentrated hydrobromic acid decomposes ethyl apocinchenic acid into homoapocinchene (5), carbon dioxide and ethyl bromide being splitoff. Sulphuric acid and manganese dioxide oxidize ethyl homoapocinchene (6) to ethyl homoapocinchenic acid (7). If the silver salt of the latter be heated, γ-quinoline phenetol (8) is formed, which is converted by hydrobromic acid into γ-quinoline phenetol (9). Apocinchene is, therefore, very probably γ,2-oxy-4,5-diethylphenyl quinoline, and apoquinene accordingly γ,2-oxy-4,5-diethylphenylmethoxyquinoline.

$$\begin{array}{c} C_{9}^{(1)} H_{6} N. C_{6} H_{2} \begin{cases} C_{2} H_{5} \\ C_{3} H_{5} \\ C_{2} H_{5} \end{cases} & \rightarrow C_{9}^{(2)} H_{6} N. C_{6} H_{2} \begin{cases} CO_{7} H \\ CH_{7} . CH_{3} \\ O. C_{7} H_{6} \end{cases} & \rightarrow C_{9}^{(3)} H_{6} N. C_{6} H_{3} \begin{cases} COO \\ CH. CH_{3} \\ O. C_{7} H_{5} \end{cases} \\ C_{9}^{(4)} H_{6} N. C_{6} H_{3} \begin{cases} COO H \\ COO H \\ O. C_{7} H_{5} \end{cases} & \rightarrow C_{9}^{(6)} H_{6} N. C_{6} H_{3} \begin{cases} CH_{7} . CH_{3} \\ OH \end{cases} & \rightarrow C_{9}^{(6)} H_{6} N. C_{6} H_{3} \begin{cases} CH_{7} . CH_{3} \\ O. C_{7} H_{6} \end{cases} \\ C_{9}^{(7)} H_{6} N. C_{6} H_{3} \begin{cases} COO_{7} H_{5} \\ OC_{7} H_{5} \end{cases} & \rightarrow C_{9}^{(6)} H_{6} N. C_{6} H_{4} OC_{7} H_{5} & \rightarrow C_{9}^{(6)} H_{6} N. C_{6} H_{4} OH \end{cases}$$

The following diagram represents the formation of γ ,0-oxydiethylphenylquinoline, or apocinchene (3), by the hydrolysis of cinchene (1), assuming the formula (2573) given above for cinchonine:

The rearrangement of the hypothetical intermediate product (2) into the phenyl-quinoline derivative finds an analogy in the transpositions of the olefine terpenes (p. 309) into hydroaromatic compounds—e. g., the production of isopulegole from citronellal (p. 308). It is probable that the breaking down of methyl cinchonine (p. 573) with methyl iodide and alkali would afford a better insight into the nature of the intermediate product (see A. 277, 277).

The synthesis of γ ,0-Oxyphenylquinoline is identical with that of γ -quinoline phenol from apocinchene. It presupposes that of salicylic acid. The diethyl ester of salicylic acid (1), acetic ester, and sodium form 0-ethoxybenzoylacetic ester (2), which is converted by boiling dilute sulphuric acid into 0-ethoxyacetophenone (3). Acetic ester and sodium ethylate transpose the latter compound into 0-ethoxybenzoyl acetone (4), from which 0-ethoxybenzoylacetone-mono-anil (5) is obtained by digesting it with acetic acid and aniline. This anil condenses to γ ,0-ethoxyphenylsulphonic acid quinaldine (6) on treating it with concentrated sulphuric acid. It he sulpho-acid be boiled with concentrated hydrotronic acid, γ ,0-exyphenylquinaldine (7) will result, and potassium permanganate will oxidize its benylidene compound (8) to γ ,0-exyphenylquinaldic acid (9). The latter decomposes at 250° into carbon dioxide and γ ,0-exyphenylquinoline (10), identical with the γ -phenylquinoline prepared from apocinchene (Besthorn and Jacque, B. 27, 3035):

(5)
$$\begin{array}{c|c} C_{\mathbf{g}}H_{\mathbf{4}}.O.C_{\mathbf{2}}H_{\mathbf{5}} \\ CO \\ CO \\ CH_{\mathbf{3}} \\ C.CH_{\mathbf{3}} \\ \end{array}$$

$$\begin{array}{c|c} C_{\mathbf{g}}H_{\mathbf{3}} & SO_{\mathbf{3}}H \\ OC_{\mathbf{2}}H_{\mathbf{5}} \\ C \\ CH \\ C.CH_{\mathbf{3}} \\ \end{array}$$

$$\begin{array}{c|c} C_{\mathbf{g}}H_{\mathbf{4}}OH \\ C.CH_{\mathbf{3}} \\ \end{array}$$

Strychnos Bases .- In the fruit of the different strychnos, principally in that of . Strychnos nux vomica and in St. Ignatius' bean (Strychnos Ignatii), are found two very poisonous bases: Strychnine and brucine. Their constitution is undetermined. They were discovered (1818 and 1819) by Pelletier and Caventou.

Strychnine, $C_{21}H_{22}N_2O_2$, melting at 284° and boiling at 270° (5 mm.) (B. 19, R. 30), is lævorotatory, reacts alkaline, has an extremely bitter taste, and occasions tetanus. Its most closely allied transposition products indicate that the one nitrogen atom belongs to a hydrogenized quinoline or indol ring and that it has sacrificed its basic character by union with a CO-group. Gradual oxidation with dilute and concentrated sulphuric acid converts strychnine into picric acid and an acid, $C_{10}H_8N_8O_8$, which splits off CO_9 when heated with water and very probably yields a dinitrodioxyquinoline, $C_0H_3N(NO_2)_2$.

(OH)₃ (Tafel, B. 26, 333).

Brucine, C₃₃H₃₆N₃O₄ + 4H₂O, melts at 178° when anhydrous. It is levorotatory.

When fused with caustic potash it yields, in addition to lutidines and collidines, tetrahydroquinoline (B. 18, R.

73; 20, 460, 813).
It dissolves with a red color in concentrated nitric acid. On application of heat it

becomes yellow and violet after the addition of stannous chloride.

The veratrum alkaloids occur, together with veratric acid (p. 228), in the white hellebore (from V. album) and in the sabadilla seeds (from V. Sabadilla). Crystalline Veratrine (B. 25, R. 284), or cevadine, $C_{32}I_{49}NO_9$, melts at 202°. It dissolves in concentrated sulphuric acid with a yellow color, which gradually changes to blood-red. It yields β -picoline (B. 23, 2707) by dry distillation.

IV. THE ISOCUINOLINE GROUP OF THE ALKALOIDS.

Opium Bases.—In opium, the dried juice of the green seed capsules of poppy (Papaver somniferum), we find not only meconic acid and meconine (p. 235), but a series of bases, of which may be mentioned:

Morphine, C₁₇H₁₉NO₃ (9 per cent.) Codelne, C₁₈H₂₁NO₃ (0.3 per cent.) Thebaine, C₁₈H₂₁NO₃ (0.4 per cent.) Papaverine, $C_{20}H_{21}NO_4$ (0.8 per cent.) Narcotine, $C_{22}H_{23}NO_7$ (5 per cent.) NarceIne, $C_{22}H_{27}NO_8$ (0.2 per cent.).

The constitution of papaverine, narcotine, and narceine remains unexplained. The nature of morphine, the principal base of opium, and its associates, codeine and thebaine, is not certainly known.

probably not isoquinoline bodies, but are treated, however, with the other Morphine is the most important of them from a medical opium bases. point of view.

Morphine, $C_{17}H_{19}NO_2 + H_2O_2$, crystallizes from alcohol in small prisms, tastes bitter, and in small quantities produces sleep. It shows an alkaline reaction, and represents a tertiary, monacid base. Its officinal hydrochloride, C₁₇H₁₉NO₂HCl + 3H₂O, forms delicate, silky needles. It is used to relieve pain and to produce sleep.

The solutions of morphine and its salts are colored dark blue by ferric chloride; the solution in concentrated sulphuric acid acquires a blood-red coloration on the addition of solution in concentrated suprime acid acquires a blood-fed coloration on the acidian at a little nitric acid. It is readily oxidized, two molecules uniting, with the exit of two hydrogen atoms, to pseudomorphine, (C₁₇H₁₈NO₃)₂ (A. 294, 206). It contains two hydroxyl groups, and deports itself as a dihydric phenol, forming salts with one metal atom, but yielding diacidyl derivatives. It forms phenanthrene on distillation with zinc-dest. Apomorphine, C₁₇H₁₇NO₃, results when water is split off from morphine by heating the latter with concentrated hydrochloric acid to 140–150°. Its hydrochloride is applied

in the liberation of mucus.

Codeine, Methyl Morphine, $C_{17}H_{17} \binom{OH}{O. CH_3}$ NO, melting at 150°, is contained in opium, and is obtained from morphine by means of methyl iodide and potassium hydroxide (B. 14, 1413).

Codeine isolmethylate, which is also produced from morphine methyl hydroxide (Const. B. 30, 354) and methyl iodide, yields, upon heating with alkali, the so-called methylmorphimethine, melting at 118°. When this is digested with acetic anhydride it is resolved into acetoxymethoxyphenanthrene and acetoxyethyldimethylamine (B. 26, R. 494; 27, 1144):

Apocodeine is obtained, like apomorphine, from morphine.

Thebaine, $C_{19}H_{21}NO_3 = C_{17}H_{15}(OCH_3)_2NO$, consists of silvery plates, melting at 103°. It breaks down into $2CH_3C$ and morphothebaine, when heated with concentrated hydrochloric acid. This new isomeric base melts at 191° (B. 27, 2961).

Thebaine or its iodinethylate is decomposed, like codeine, on boiling with acetic anhydride, into acetylthebaol, an acctoxydimethoxyphenanthrene and oxethylmethylamine:

$$\begin{array}{c} \text{CH}_{3}\text{O} \\ \text{CH}_{3}\text{O} \end{array} \xrightarrow{\text{C}_{14}\text{H}_{3}} \begin{array}{c} \text{O} \\ \text{C}\text{CH}_{3}\text{O} \\ \text{Thebaine} \end{array} \xrightarrow{\text{CH}_{3}\text{O}} \begin{array}{c} \text{CH}_{3}\text{O} \\ \text{CH}_{3}\text{O} \\ \text{Dimethoxy-oxyphenanthrene} \end{array} \xrightarrow{\text{CH}_{3}\text{O}} \begin{array}{c} \text{CH}_{1}\text{OH} \\ \text{CH}_{3}\text{NH} - \text{CH}_{1} \\ \text{Oxethylmethylamine.} \end{array}$$

Boiling dilute hydrochloric acid changes thebaine, a tertiary base, into the secondary base Thebenine, C₁₇H₁₅(OH)(OCH₃)NO. When this is treated with ethyl iodide and decomposed with caustic potash, methyldiethylamine and thebenol, C₁₆H₁₀(OCH₃)(OH), result. Pyrene (p. 420) (B. 30, 1357) is produced in the distillation of thebenol with zinc dust.

Papaverine (1), Tetramethoxybenzylisoquinoline, C₂₀H₂₁NO₄, melts at 148°. Its constitution becomes evident from its decompositions. Hot hydriodic acid decomposes it into 4CH₂I and the base papaveroline (2). Potassium permanganate oxidizes it to papareraldine (3), or tetramethoxybenzoylisoquinoline.

Papaverine breaks down into veratric acid (5) and dimethylisoquinoline (4) when

fused with caustic potash.

The oxidation of papaveraldine gives rise to papaveric acid, a-dimethoxylbenzoyl-pyridine- β ,y-dicarboxylic acid (6), dimethoxylsoquinoline carboxylic acid (7), α , β ,y-pyridineitricarboxylic acid (8), and metahemipinic acid (9) (G. Goldschmidt, B. 21, R. 650). Compare the following diagram. The hydrogen atoms are omitted from the rings in order that the representation may be clear:

Narcotine (1), Meconinehydrocotarnine, C₂₂H₂₂NO₃, melting at 176°, is separated from morphine by potassium hydroxide, in which it is insoluble (1817, Robiquet). Boiling water decomposes it into cotarnine (2), melting at 132° (1844, Wöhler, A. 50, 1), an amidoaldehyde and meconine (p. 235) (3). The latter yields opianic acid (p. 237) and hemipinic acid (p. 242) on oxidation.

Cotarnine is an aldehyde. It forms salts with acids, water being eliminated and the isoquinoline ring being closed. Cotarnine upon reduction becomes hydrocotarnine (4), while potassium permanganate oxidizes it to cotarnic acid (5), a methylmethylenetrioxybenzene dicarboxylic acid, which yields methylmethylenegallic acid (6) on being heated with hydrochloric acid, and gallic acid with hydriodic acid (W. Roser, A. 249, 156; 254, 334; 272, 221). Nitric acid oxidizes cotarnine to apophyllenic acid (7) (see B. 29, 2190). It must be observed that the position assumed, in the following formulas, for the dioxymethylene and methoxy-groups in the isoquinoline nucleus is wholly arbitrary:

In the attempt to prepare narcotine by condensing opianic acid and hydrocotanine with sulphuric acid an isomeric isonarcotine, melting at 194°, resulted. It may be recognized by the red coloration it gives with concentrated H₂SO₄ (B. 29, 183, 2040).

Narceine (2), $C_{23}H_{27}NO_8 + 3H_2O$, melting at 170°, and when anhydrous at 140-145°, occurs, together with narcotine, in opium, and is formed when the iodmethylate (1) of narcotine is acted upon with caustic potash (A. 286, 248):

Hydrastine (1), $C_{31}H_{31}NO_{4}$, melting at 132° , $[a]_{D} = -67^{\circ}$ in chloroform (1851, Durand), occurs, together with berberine, $C_{30}H_{17}NO_{4} + 5\frac{1}{2}H_{2}O$, melting at 120° (it is found with hydrastine in *Berberis vulgaris*), in the roots of *Hydrastis canadensis*, a North American plant belonging to the Ranunculaceæ. It is constituted similarly to narcotine. When acted upon by oxidizing agents it breaks down into opianic acid (3) (p. 237) and hydrastinine (2), melting at 116°, which carries the hydrastine. Hydrastine, like cotarnine, is an aldehyde. Reducing agents convert it into the corresponding alcobol, which at once loses water and becomes hydrohydrastine (4), Bz-2,3-methylenedioxytetrahydroisoquinoline. Potassium permanganate oxidizes hydrastinine first to oxyhdrastinine (5), then to hydrastinine acid, which nitric acid converts into the methyl imide of hydrastic acid (6) or normetahemipine-methylene ether acid. Hydrastinine itself, like cotarnine, is oxidized by nitric acid to apophyllenic acid (6). The isoquinoline ring is present in the salts of cotarnine and hydrastine. The formation of salts follows in consequence of the exit of water (W. Roser, A. 249, 172; Freund, A. 271, 311):

The synthesis of hydrastinine was effected in the following manner: Piperonal-acetalamine (1) condenses with sulphuric acid to Bz-2,3-methylenedioxyisoquinoline, melting at 124° and boiling at 215° (50 mm.), which becomes hydrohydrastinine (see above), melting at 60-61°, upon reducing its iodmethylate (3), melting at 244°, with tin and hydrochloric acid. Potassium bichromate and sulphuric acid change the hydroderivative back to hydrastinine (Fritsch, A. 286, 18):

$$(1) \qquad H \qquad CH \qquad (2) \qquad H \qquad CH \qquad (3) \qquad H \qquad CH$$

$$CH_{2} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow CH$$

$$CH_{3} \longrightarrow CH_{2} \longrightarrow CH_{2} \longrightarrow CH$$

$$CH_{4} \longrightarrow CH_{2} \longrightarrow$$

Berberine is even more complex in its constitution than hydrastine. The constitutional formula, here presented, has been deduced from its decomposition reactions (Perkin, Jr., B. 24, R. 157). The position of the dioxymethylene group in this formula is based upon the synthesis of oxyhydrastinine from the decomposition products of berberine. The constitution of oxyhydrastinine has been determined by its conversion into hydrastic acid.

B. POLYHETERO-ATOMIC SIX-MEMBERED RINGS.

AZINES.

Polyhetero-atomic six-membered rings, containing oxygen and sulphur as ring members, occur in a series of bodies which have already been discussed at the conclusion of allied bodies. Dialkylen ethers—e.g., diethylene oxide (1, 298)—and the anhydrides of a-oxyacids—e.g., glycollide, diglycollic anhydride (1, 339)—contain rings consisting of four carbon atoms and two oxygen atoms. The six-membered ring of diethylene disulphide (1, 305), and of thianthrene or diphenylene disulphide (11, 518), contains two sulphur atoms, while three oxygen atoms or three sulphur atoms are present in the polymeric aldehydes and the thioaldehydes—e.g., trioxymethylene, trithiomethylene, paraldehyde, trithioaldehyde (1, 194, 203), etc. (see 11, 441).

Those members of this division containing N-atoms as ring members require more exhaustive consideration. This was done also with like bodies of the five-membered series. They may be regarded, like the azoles, as derived from furfurane, thiophene, and pyrrol by the replacement of methine groups of monoheteroatomic rings, and accordingly they can be grouped under the common name of azines.

The oxazines, oxdiazines (azoxazines), and dioxdiazines are then the rings with the hetero-atoms: N and O, 2N and O, 2N and 2O; the thiazines and thiodiazines (diazthines) are the rings with the hetero-atoms S and N, S and 2N, and the diazines, triazines, and tetrazines are the sixmembered rings with 2, 3, and 4 N-atoms. The place isomerides of diheteroatomic azines are distinguished according to the position of the hetero-atoms with reference to one another by the prefixes ortho-, meta-, and para-. Thus, the three possible diazines as orthodiazine,

(B. 22, 2083; A. 249, 1; J. pr. Ch. 38, 185); the oxazines as orthoxazines, metoxazines, paroxazines; the thiazines as orthothiazines, metathiazines, and parathiazines.

The parent substances of important classes of dyes: compare rumfin, methylene blue, toluylene red, safranines, indulines, are the dibentoderivatives of the paroxazines, parathiazines, and paradiazines.

I. OXAZINES.

A. The ring of orthoxazine,
$$c - c - b$$
, is present in the oxime anhydrides of the

y-aldehydo- and y-ketonic acids—e. g., benzal favoxime, C₈H₃CH: CH = CH₇ = CO

(p. 288), which bear the same relation to the oxime anhydrides of the β-ketonic scid, the isoxazolons (p. 495), as the d-lactones to the y-lactones (B. 25, 1930). The ring formation of the oximes of o-benzaldehyde and o-benzo-ketone carboxylic acids occas

without difficulty. Derivatives of benzorthoxasines are produced: Benzorthoxasinon, o-Benzaldoxime carboxylic anhydride, C_8H_4 C_{CO} , is derived from phthalaldehydic

acid (p. 236). It readily rearranges itself to the isomeric phthalimide (B. 24, 2347). There is an intermediate formation of o-cyanbenzoic acid (see the indoxazenes, p. 495). Benzomethylorthoxazinon, o-Acetophenonoxime carboxylic anhydride,

$$C_8H_4$$
 $CO \longrightarrow O$ melts at 179° (B. 16, 1995, and p. 238).

B. The following contain the Metoxazine ring, $\beta \stackrel{c}{C} = \stackrel{c}{C} = \stackrel{c}{C} = \stackrel{c}{C}$

I. The pentoxasolines, which are produced by the splitting-off of HBr from the y-bromalkylamides. This is similar to the formation of the five-membered oxazolines (p. 503) from the β -bromalkylamides (B. 24, 3213):

$$\begin{array}{c} \text{CH}_{2}\text{--CH}_{2}\text{--NH} \\ \downarrow \\ \text{CH}_{3}\text{Br} \quad \text{OC} \cdot \text{C}_{4}\text{H}_{5} \\ \gamma \text{--Bromethylbenzamide} \end{array} \longrightarrow \begin{array}{c} \text{CH}_{3}\text{--CH}_{3}\text{--N} \\ \downarrow \\ \text{CH}_{2}\text{--O} \quad \text{--CC}_{4}\text{H}_{5} \\ \mu \text{--Phenylpentoxazoline}. \end{array}$$

 μ -Phenyl-a-methyl Pentoxazoline, $C_aH_aNO(CH_3)(C_8H_5)$, and μ -Phenyl-a-dimethyl- γ -methyl Pentoxazoline, $C_aH_3NO(CH_3)_s(C_8H_8)$, melting at 32°, are obtained from γ -chlorbutyl- and γ -bromisohexylbenzamide.

μ-Allylamido- and μ-phenylamido-γ-methyl Pentoxazoline, or n-allyl and CH, —— CH, — N n-phenyl butylene-\(\psi\)-urea, | CH(CH₃) = O \(\bigcup_{\text{C}} \bigcup_{\text{C}}

amine by means of allyl- and phenyl-mustard oil (B. 29, 1428; 30, 1319).

Derivatives of benzometoxazine or phenoentoxasoline are formed from o-amido-benzylhalogenides (p. 180) and acid anhydrides (B. 27, 3515):

$$\begin{array}{c} {\rm C_6H_4 < \stackrel{CH_9Br}{NH_2} + \ HOOC.\ CH_3 \longrightarrow C_6H_4 < \stackrel{CH_9-O}{N \stackrel{}{=} \stackrel{C}{C}.\ CH_3} } \\ {\rm o-Amidobenzyl\ Bromide} \\ \end{array} } \\ \begin{array}{c} {\rm c-Amidobenzyl\ Bromide} \end{array}$$

The commazonic acids (p. 236 and B. 16, 2585) also belong here—e. g., μ -Methyl Coumazonic Acid, Benzotrimethylmetoxasine, $C_0H_4 < N - C$. CH₃)₂—C. CH₃, melting at 218°, and µ-Phenyl Coumazonic Acid, Bensodimethyl-u-phenylmetoxassine, C_6H_4 $C(CH_3)_2 = O$ C_6H_6 , melting at 220°, which have been obtained from 3 amido4-oxypropylbenzoic acid with acetyl chloride and benzoyl chloride. Carbon dioxide is liberated.

The imido- and thio-commasones are derivatives of dihydrobenzometoxasine. former result upon the exit of water from the urea derivatives of o-amidobenzyl alcohol (p. 185), the latter by the action of CS, upon the alcoholic solution of o-amidobenzyl alcohol and related compounds:

The imido-coumazones are isomeric with the keto-tetrahydroquinazolines (p. 592),

and when digested with aromatic amines become quinazoline compounds (p. 589). The O-member is replaced by NR. The thiocoumazones behave similarly (B. 27, 2424).

Phenylimidocoumazone, Benzodihydrometoxazine anil, C₈H₁ON: (NC₈H₅), melting at 146° (B. 22, 2938), forms stable salts with acids; with acid anhydrides and chlorides it yields addition products. Thiocoumazone, Benzodihydrothiometoxasine, C.H.ON: S, melting at 142°, is an acid, and forms a sparingly soluble potassium salt (B. 25, 2979; 27, 1866).

N.—C.—C.
C. Paroxazines, C.—C.—O: I. Only saturated derivatives of the simple nucleus

are known. The following are tetrahydroparoxazines: Morpholine (1, 310) and its alkylic compounds. n-Benzyl Morpholine, boiling at 261°, is produced from dibromethylbenzylamine, and also from chlorethylbenzylamine (B. 24, R. 821; 29, 2386). Diglycollo-imide and the derivatives of isomeric diglycollamid-anhydride (B. 25, 2272) are diketotetrahydroparoxazines:

- II. Benzoparoxazine yields: β -Phenylbenzoparoxazine, $C_6H_4 < N \dot{C} \cdot C_6H_5$ melting at 103°, and β -methylbenzoparoxazine. They are obtained by the reduction of o-nitrophenylphenacyl ether, $C_6H_4 < O \cdot CH_2 \cdot CO \cdot C_6H_5$, and o-nitrophenacetal (B. 23, 172). Benzomorpholine, $C_6H_4 < O CH_2 \cdot CH_2$, boiling at 268°, is made from o-oxethyl-
- amidophenol (p. 152). Benzoketomorpholine, C₆H₄<0 CO NH CII, is produced by reducing glycol-o-nitrophenyl ether acid, CaH4(NO2)OCH2COOH (B. 20, 1943).
- III. The group of dibenzoparoxazine or phenoxazine, benzonaphtho-, and dinaphthoparoxazine has been more fully developed. A series of important dyes belongs to it:

Phenoxazine, C₆H₄<0/NI>C₆H₄, melting at 148°, is produced on heating o-amidophenol with pyrocatechol (p. 160).

The dyes of the phenoxazine group contain quinone unions (p. 167). They may also be regarded as quinone anils, indophenols, or indamines (p. 174), in which the two nuclei are further united by an oxygen atom in the ortho-position with reference to the tertiary nitrogen:

$$\begin{aligned} \text{O:} & \text{C}_{\textbf{6}} \text{II}_{\textbf{4}} = \text{N--} \text{C}_{\textbf{6}} \text{II}_{\textbf{4}} \text{OH} & \text{O:} & \text{C}_{\textbf{6}} \text{II}_{\textbf{3}} \overset{\text{N}}{\searrow} \text{C}_{\textbf{6}} \text{H}_{\textbf{3}} \text{OH} \\ & \text{Indophenol} & \text{Oxyphenoxazone (Resorufin).} \end{aligned}$$

The parent bodies of the phenoxazine dyes are distinguished as phenoxazones, or phenoxazines (B. 25, 2995), depending upon whether they are quinone-monimide or di-imide derivatives. They are produced:

1. Upon condensing o-oxyquinones and o-oxyquinone-imides with o-amidophenols. The oxy-p-quinones of the naphthalene series are mainly best adapted for these condensations (B. 26, 2375; 28, 353):

$$O: C_{10}H_{6} \bigcirc OH \\ OH \\ H_{2}N \bigcirc C_{6}H_{6} \longrightarrow O: C_{10}H_{6} \bigcirc OC_{6}H_{6}$$
a.o-Oxynaphthoquinone o-Amidophenol Naphthophenoxazone.

Oxy- and amido-derivatives of the phenoxazones and phenoxazimes, the real dyes, result by the condensation of quinone dichlorimides, nitrosophenols, or nitrosodimethyl aniline with polyhydric phenols or tertiary amidophenols:

Resorufin, Oxyphenoxazone, O: C₈H₈(NO)C₆H₈(OH), is produced when nitric acid containing N2O3 acts upon an ethereal solution of resorcinol (p. 160) (Weselsky, A. 162, 273); and from nitrosoresorcinol by means of resorcinol (B. 24, 3366). Resa-

A. 162, 273); and from nitrosoresorcinol by means of resorcinol (B. 24, 3300). Keiazurine, O: C₆H₃(NO) C₆H₃(OH), is an intermediate product in this reaction. The alkaline solutions of resorufin are rose-red, with a magnificent cinnabar-red fluorescence. Orcirufin is obtained, like resorufin, from orcinol (p. 162). Gallocyanine, Dimethylanido-oxyphenoxacon-carboxylic acid, N(CH₃)₂, C₆H₃(NO)C₈H(OH)COOH: O, is produced by the action of nitrosodimethylaniline upon gallic acid (p. 230). With mordants, especially chromic oxide, it forms violet-colored and stable lakes (calico printing). Chloroxydiphenoxazone, C₈H₄(NO)C₈HCl(OH): O, melting with decomposition at 235°, is obtained from p-dioxychlorquinone and amidophenol (B. 26, 2375).

Naphthophenoxazone, O = C₁₀H₅(NO)C₈H₄, melts at 192°. Naphthophenoxazone, NH: C₁₀H₅(NO)C₈H₄, melts at 192°. Naphthophenoxazone, imide (p. 407).

naphthoquinone imide (p. 407).

Dimethyl Naphthophenoxazime Chloride, $C_{10}H_6(NO)C_6H_3$: $N(CH_3)_3Cl$, from β -naphthol and nitrosodimethyl aniline, is the so-called *naphthol blue*, which dyes cotton mordanted with tannin a violet-blue (B. 23, 2247). *Nile blue* is an amido-derivative of naphthol blue, while *cyanamine* is an anilido-derivative. For other derivatives consult A. 289, 90; B. 29, R. 1000).

Oxyphenoxazime, C6H4 NC6H12 NH, results from the oxidation of o-amido-

It condenses to triphendioxazine, C_6H_4 $\stackrel{N}{\bigcirc}$ C_6H_4 , with another molecule of amidophenol (p. 153; B. 23, 182; 27, 2784). See B. 29, 2076, for methyl triphendioxazine.

2. THIAZINES.

A. Orthothiazines:
$$\begin{array}{c} C - C - N \\ \dot{C} - C - \dot{S} \end{array}$$
, are not known (a)C - N - C(μ)

ring:

I. The penthiazolines, corresponding to the pentoxazolines. They are prepared from the y-haloid alkylthiobenzamides.

CH₂. CH₃. N

μ-Phenyl Penthiazoline,
CH₃. S — C. C₆H₅

thiobenzamide (p. 204) and trimethylene chlorbromide (B. 26, 1077). μ-Phenyl-adimethyl-γ-methyl Penthiazoline, C₄H₂NS(CH₃)₈(C₆H₅), melting at 34°, is derived
from γ-bromisoloxylthiobenzamide. μ-Mercapto γ-methyl Penthiazoline and γmethyl-a-dimetyl-penthiazoline, melting at 131° and at 180°, are made from
γ-chlorbutylamine and γ-bromisoloxylamine by the action of carbon bisulphide (B. 29,
1429; 30, 1321; see also B. 29, R. 648 and 684).

Diketopenthiazolidine, Sinapan-propionic Acid, $CH_2 - CO - NH$, melting at 159°, results when β -iodpropionic acid acts upon xanthogenamide (B. 24, 3848).

II. Derivatives of bensometalhiasine or phenoenthiasole are produced in the interaction of o-amidobenzyl haloids and carbon-thiamides (pp. 180, 204) (B. 27, 3519):

$$C_0H_4{<}^{CH_3Br}_{NH_4} + NH_2CS.CH_3 \longrightarrow C_0H_4{<}^{CH_3-S}_{N \longrightarrow \mathring{C}.CH_3}.$$

 μ -Methyl Phenpenthiazole, melting at 46°, is produced by the action of P_2S_5 upon μ -methyl phenpentoxazole; also from o-acetylamidobenzyl alcohol and P_2S_5 , as well as from o-acetylamidobenzyl sulphide and PCl_5 . Consult B. 30, 1143, for other derivatives.

The imido- and thio-coumothiazones, corresponding to the imido- and thiocoumazones, belong here. Like them, they result from the action of CS, and alcoholic potash upon the thio-urea derivatives of o-amidobenzyl alcohol—or amidobenzyl alcohols in general (p. 180):

Thiocoumothiazone, Bensodihydrothiothiazine, C₆H₄ < CH₂ - S, melting at 166°, is an acid. It forms n-phenylthiotetrahydroquinazoline when boiled with aniline, the ring sulphur atom being replaced by NC₂H₈ (pp. 581, 592). Imido-coumothiazone,

ring sulphur atom being replaced by NC₆H₅ (pp. 581, 592). Imido-coumothiazone,

NH — C:NH

Benzylene-ψ-thiourea, C₆H₄ < CH₂ — S

CH₂ — S

CH₃ — S

characteristic for introduced and sulpharent are replaced as well as from a smide

is produced in the reduction of o-nitrobenzyl sulphocyanide, as well as from o-amido-benzyl chloride and thiourea. Potassium permanganate oxidizes it to a-quinazolon, while digested with aniline it forms phenylimido-coumothiazone, benzodihydrothiazine amil, melting at 197°, which results upon expelling water from o-oxytolylphenylthiourea (B. 22, 2933; 27, 2429).

(B. 22, 2933; 27, 2429).

C—N—C

C. Parathiazine, C—S—C: Ketodihydrobenzothiazine, C₆H₄ < S—CH₃, is a benzo-derivative which may possibly originate from this ring. It melts at 179°, and is produced by the interaction of o-amidothiophenol and brom-acetic acid (B. 30, 607).

The symmetrical dibenzo-derivatives—e. g., dibenzo- and dinaphtho-parathiazine, or thiodiphenylamine (p. 80), and thiodinaphthylamine (p. 396)—are more important. Thiodiphenylamine corresponds to phenoxazine or dibenzoparoxazine (p. 581), and, like the latter, is the parent substance of a series of more important dyes, among which is the very valuable methylene blue.

Thiodiphenylamine, $C_0H_4 < \sum_{NII} > C_0H_4$, melting at 150° and boiling at 370°, is prepared analogously to phenoxazine by heating o-amidothiophenol and pyrocatechol to 220°. An easier course consists in heating diphenylamine to 250° with sulphur or S₂Cl₂ (B 21, 2063). It is a neutral body, the imide hydrogen of which can be replaced by alkyl and acid radicals. See B. 24, 2910, for the urea derivatives. Tetrachlor-

thiodiphenylamine melts at 235° (B. 29, 1363). Nitric acid oxidises thiodiphenylamine to nitrodiphenylamine sulphoxide, $C_6H_4 < \frac{SO}{NH} > C_8H_8NO_9$, which can be reduced to amidothiodiphenylamine. The reduction of dinitrodiphenylsulphoxide yields Diamidothiodiphenylamine, Leucothionine, NH_2 . $C_6H_3 < \frac{S}{NH} > C_6H_8NH_9$, which is produced on heating p_3 -diamidodiphenylamine, $(NH_3C_6H_4)_3NH$, with sulphur. It is the leuco-base of the simplest thionine dye into which it can be converted by oxidation with ferric chloride. The tetramethyl derivative of leucothionine is the leuco-base of methylene blue (see below).

The dye-substances of the thiodiphenylamine group contain quinone unions. Like the paroxazine dyes, they are to be viewed as indophenol and indamine derivatives, in which the two phenyl groups are further united by sulphur:

NH₂.
$$C_6H_4$$
—N = C_6H_4 : NH \xrightarrow{S} NH₂. C_6H_3 \xrightarrow{N} C_6H_8 = NH

Phenylene Blue (p. 174)

Lauth's Violet.

The phenthiasimes and phenthiasones, like the phenoxazimes and phenoxazones, are distinguished according as they represent quinonediimide or monimide derivatives. Lauth's dye-substances belong to the phenthiazimes (Bernthsen, A. 230, 73; 251, 1). They result upon oxidizing paraphenylenediamines in the presence of hydrogen sulphide. It is probable that indamines occur as intermediate products (p. 174):

$$2\mathrm{NH}_{1}\mathrm{C}_{8}\mathrm{H}_{4}\mathrm{NH}_{2} \xrightarrow{-+\frac{S}{-SH}} \mathrm{NH}_{2}\mathrm{C}_{8}\mathrm{H}_{5} \diagdown^{N}_{S}\mathrm{C}_{8}\mathrm{H}_{5}:\mathrm{NH}.$$

Another procedure which may be adopted in the preparation of these dyestuffs is based upon the fact that indamines and thiosulphuric acid yield thiosulphonic acids, which change to the leuco-bases of the thiazine dyestuffs upon boiling them with dilute acids. Therefore, the dyestuffs can be obtained by oxidizing a mixture of one molecule of p-diamine with one molecule of a monamine, which form the indamine, in the presence of a thiosulphate. Thiazones are produced when p-amidophenols are oxidized in the presence of hydrogen sulphide.

Amidophenthiazine, Thionine, Lauth's Violet, NH₂, C₆H₃(NS)C₆H₃: NII, is obtained from p-phenylenediamine, and also from its leuco-base, diamidothiodiphenylamine, by oxidation.

Methylene Blue, Tetramethylamidophenthiazimium chloride, (CH₃)₄-N. C₆H₃(NS)C₆H₃: N(CH₃)₄Cl (Caro, 1877), results upon oxidizing two molecules of dimethyl-p-phenylenediamine in H₂S-solution, or one molecule of dimethyl-p-phenylenediamine with one molecule of dimethyl aniline and thiosulphate.

It dyes silk, or cotton mordanted with tannic acid, a beautiful fast blue.

Phenthiazone, C₆H₄(SN)C₆H₃O, results upon oxidizing oxythio-diphenylamine. Oxyphenthiazone, Thionol, HO. C₆H₃(NS)C₆H₃: O, is produced on boiling thionine with dilute acids or alkalies.

3. DIAZINES.

A. Orthodiazines,
$$\begin{pmatrix} (4) & (3) \\ C & C & N \end{pmatrix}$$
 (2) $\begin{pmatrix} 1 & (2) \\ C & C & N \end{pmatrix}$ (2): I. Orthodiazine or Pyridazine, $\begin{pmatrix} C_4H_4N_2 \\ C_3 \end{pmatrix}$ (5) (6)

melting at 8° and boiling at 208°, may be prepared from its tetracarboxylic acid, the exidation product of dibenzorthodiamine or phenazone (p. 587):

Pyridazine is an oil with an odor like that of pyridine. It forms very soluble salts, addition compounds with AuCl₃, HgCl₃, etc. Pyridazine Dicarboxylic Acid, C₂H₂N₂(CO₂H)₂, melting with decomposition at 205°, is obtained from the dipotassium malt of the tetracarboxylic acid.

3,4,6-Triphenyl Pyridazine, C4H(C6H5)2N2, melting at 171°, is readily produced

by exidizing its dihydro-derivative.

Dikydropyridasines are formed from the 1,4-diketones and hydrazines, either without er together with the n-amidopyrrols, which are to be expected:

$$\begin{array}{c} C_{e}H_{5}. CH -CO.C_{e}H_{5} \\ CH_{2}-CO.C_{e}H_{5} \end{array} + NH_{2}. NH_{3} \longrightarrow \begin{array}{c} C_{e}H_{5}C == C(C_{e}H_{5}) - NH \\ CH = C(C_{e}H_{5}) - NH \end{array}$$

3.4.6-Triphenyldihydropyrazine, melting at 187°, becomes pyridazine, by heating it or by treating it with chromic acid. 1,3,4,6-Tetraphenyldihydropyridazine, $C_4H_2(C_9-H_2)_4N_2$, melting at 149°, is obtained from desylacetophenone and phenylhydrazine. It yields 1,3,4-triphenylpyrazole (p. 483) (A. 289, 310) upon dry distillation:

$$\begin{matrix} C_{\textbf{e}}H_{\textbf{5}}C & == & C(C_{\textbf{e}}H_{\textbf{5}}) - NH \\ \downarrow & \downarrow & \downarrow \\ CH & = & C(C_{\textbf{e}}H_{\textbf{5}}) - N(C_{\textbf{e}}H_{\textbf{5}}) \end{matrix} \longrightarrow \begin{matrix} C_{\textbf{e}}H_{\textbf{5}}C - & C(C_{\textbf{e}}H_{\textbf{5}}) \\ \parallel & \parallel \\ CH - & N(C_{\textbf{e}}H_{\textbf{5}}) \end{matrix} \nearrow N.$$

See below for the ketodihydropyridazines or pyridazones.

The ring-homologues of the pyrazolones are ketotetrahydropyridazines or pyridazinones (B. 28, R. 68), and as these are formed from the hydrazones of β -ketonic esters, so the pyridazinones are prepared from γ -ketonic ester hydrazones (p. 126):

$$\begin{array}{c} CH_{2}-CH_{2}\cdot COOR \\ CH_{3}C=N-NH\cdot C_{6}H_{5} \\ \end{array} \xrightarrow{\begin{array}{c} CH_{2}-CO-N\cdot C_{6}H_{5} \\ CH_{2}-C(CH_{3})=N \\ \end{array}} CH_{2}-CO-N\cdot C_{6}H_{5}$$

$$\begin{array}{c} CH_{2}-CO-N\cdot C_{6}H_{5} \\ CH_{2}-C(CH_{3})=N \\ \end{array}$$

$$\begin{array}{c} CH_{2}-CO-N\cdot C_{6}H_{5} \\ CH_{2}-C(CH_{3})=N \\ \end{array}$$

$$\begin{array}{c} CH_{2}-CO-N\cdot C_{6}H_{5} \\ CH_{2}-C(CH_{3})=N \\ \end{array}$$

The pyridazinones are not so stable as the pyrazolones.

Pyridazinone, $C_4H_6ON_3$, is an oil, boiling at 170°. It results from saponification and by the removal of CO_2 from pyridazinone-3-carboxylic ester, $C_4H_6ON_2$. CO_2R , melting at 172°. This is a condensation-product of hydrazine with succinylo-formic ester, or ing at 172°. This is a condensation-product of hydrazine with succinylo-formic ester, or formyl succinic ester (B. 28, R. 239). Pyridazinone is readily decomposed by boiling alkalies, with the splitting-off of hydrazine. 3-Methyl Pyridazinone, melting at 94°, and 3-Phenyl Pyridazinone, melting at 149°, are prepared from kevulinic ester and benzoyl propionic ester. 3-Phenylpyridazinone-5-carboxylic ester, melting at 156°, is obtained from benzoyl propionic ester and hydrazine hydrate (B. 28, R. 68). I-Phenyl-3-methyl Pyridazinone, C₄H₄(CH₃)ON₂C₆H₅, melting at 107° and boiling at 340-350°, CH—CO——N. C₆H₅
yields I-Phenyl-3 methyl pyridazone,

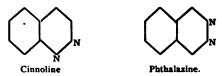
yields 1-Phenyl-3 methyl pyridazone, i CH — C(CH₃) — N

PCI, and ice-water. It contains two atoms less of hydrogen. It melts at 82°. Phenyl-methylchlorpyridazone is formed at the same time, and can be converted by NaOC₂H₅ into ethoxyphenylmethylpyridazone. This on saponification becomes oxyphenylmethylpyridazone, which sustains rearrangement into I-phenyl-3-methylpyrazole-5-carboxylic acid on being heated to 170° with hydrochloric acid (p. 485):

$$\begin{array}{c} C(OH)-CO \longrightarrow N \cdot C_0H_0 \\ CH \longrightarrow C(CH_1)=N \end{array} \longrightarrow \begin{array}{c} COOH \cdot C \longrightarrow N(C_0H_0) \\ CH \longrightarrow C(CH_1)=N \end{array} \longrightarrow \begin{array}{c} CH \longrightarrow C(CH_1) \\ CH \longrightarrow C(CH_1)=N \end{array}$$

Maleic Acid Hydrazine, \parallel , melting above 250°, is diketotetra-CH—CO—NH (H-CO-NH) which is formed, together with isomeric maleic hydrazil, or n-amidomaleinimide, from maleic anhydride and hydrazine (B. 28, R. 429). Diketokexakydro-pyridazines, or ortho-piperazones, are cyclic hydrazides of the succinic acid series, which are produced on heating the chlorides of these acids with the hydrazine hydrochlorides $(P-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-CO-N-C_0H_0-C$

II. Benzorthodiazines.—There are two isomeric benzorthodiazines, depending upon whether the benzene ring attaches itself to the C-atom (3) and (4) or (4) and (5) of orthodiazine. The cinnolines and phthalazines correspond to these two isomerides:



Cinnoline, $C_6 \Pi_4 < CH - CH \\ N - \frac{1}{N}$, melting at 39°, is a strong base. It is poisonous. Its inductivate melts at 168°.

All the cinnoline derivatives known at present have been obtained from oxycinnoline carboxylic acid, $C_6H_4[C_2N_2(OH)(COOH)]$, melting at 260°, which is produced on digesting o-phenylpropiolic acid diazochloride with water (p. 284):

$$C_6H_4{\stackrel{C-C.\,COOH}{\underbrace{N_{2}(OH)}}} \longrightarrow C_6H_4{\stackrel{C(OH)-C.\,COOH}{\underbrace{N_{----}N}}}.$$

The acid loses CO_2 and becomes oxycinnoline, $C_8H_5N_2(OH)$, melting at 225°. PCI_5 converts this into chlorcinnoline, $C_8H_5N_2CI$, the chlorine atom of which may be easily replaced by OH, OC_2H_5 , NHC_6H_5 , etc. Iron filings and sulphuric acid reduce chlorcinnoline to dihydrocinnoline, $C_6H_4(C_2H_4N_2)$, melting at 88°, which mercuric oxide oxidizes to cinnoline (B. 25, 2847; 30, 521).

Phthalazine, $C_6H_4(C_1H_4N_2)$, melting at 91°, and boiling at 316° (its chlorhydrate

Phthalazine, C_6H_4 CH := N , melting at 91°, and boiling at 316° (its chlorhydrate melts at 231°), is produced when a hydrazine solution acts upon ω -tetrachlor-, or, better, tetrabrom-o-xylene (p. 233): C_6H_4 CHBr₂ $+ H_2N$ CHBr₃ CH = N . Phthalazine and methyl iodide form an iodimethylate, $C_8H_6N_2$. ICH₃, melting at 235-240°, which silver oxide converts into n-methylphthalazone, and caustic potash into n-methylphthalazone and dihydro-n-methylphthalazine, C_8H_4 CH = N CH₂ NcH₃, which oxidizes very rapidly in the air to n-methylphthalazone (see the allied rearrangements of the alkyl quinolinium iodides (p. 544). Sodium amalgam reduces phthalazine to tetrahydrophthalazine, C_6H_4 CH₂. NH while with zinc-dust and hydrochloric acid the product is o-xylylene diamine, C_6H_4 (CH₂. NH) while with zinc-dust and hydrochloric acid the product is o-xylylene diamine, C_6H_4 (CH₂NH₂); (B. 26, 2210; 28, 1830, 2210). Chlorphthalazine, C_6H_4 (CH₂IIClN₂), melting at 113°, as well as methyl-, propyl-, and isobutyl chlorphthalazone, melting at 130° and 67° (the third being an oil), result from the action of POCl₃ upon phthalazone and alkylic phthalazones. The reduction of these chlorides

ads to derivatives of isoindol (p. 232). Thus, chlorphthalazine forms dihydroisoindol, H₄<CH₂>NII (p. 462); and methyl chlorphthalazine, methyl isoindol,

C(CH₂)N, which yields dihydromethylisoIndol upon further reduction.

Ketselikydrophthalazines, phthalazones, have been obtained from aromatic o-aldehydo-ad ketone carboxylic acids by means of the hydrazines:

$$\begin{array}{c} C_6H_4 < \begin{matrix} CHO \\ COOII \end{matrix} + \begin{matrix} H_1N \\ H_2N \end{matrix} \longrightarrow \begin{array}{c} C_6H_4 < \begin{matrix} CII = N \\ CO = NH \end{matrix} \\ Phthalaldehydic Acid \end{matrix}$$

Phthalazone, C₈H₆ON₉, melting at 183° and boiling at 337°, combines with alco-melic potash to potassium-phthalazone, C₈H₆ON₂K. Acetyl chloride converts it into pacetyl-phthalazone, while methyl iodide converts it into phthalazine iodmethylate.

-

e-Methyl Phthalazone, $C_0H_4 < CO - NH$, melting at 220° and boiling at

28°, is obtained from o-acetophenone carboxylic acid (B. 26, 524, 535). c-Propyl-, cobutyl-, and Benzyl Phthalazone melt at 156°, 113°, and 152° (B. 29, 1434).

The cyclic hydrazides of the o-phthalic acids are diketophthalazines. They cor-

respond to the orthopiperazones (p. 585), and can therefore be designated benzortho- CO - NHrelating beyond 250°, results CO - NH CO - NH CO - NH

the action of hydrazine upon phthalic ester, chloride, or anhydride (J. pr. Ch. [2], 447; 54, 66). Phthalyl Phenylhydrazine (p. 240) results when phthalyl phenyl-

reduced with sodium amalgam and methyl alcohol, an intramolecular formation of the azoroup occurs:

$$C_aH_a \stackrel{NO_a O_bN}{\sim} C_aH_a \longrightarrow C_aH_a \stackrel{N}{\sim} C_aH_a$$

Phenazone dioxide and phenazone monoxide are intermediate products. Phenazone also formed on heating diphenylene-o₂-dihydrazine with hydrochloric acid to 150°. Dihydrophenazone, C₁₂H₆(N₂H₂) (B. 24, 3083), is formed in the reduction of phenamone with tin and hydrochloric acid.

Phenazone is isomeric with phenazine (p. 598). It may also be regarded as derived from phenanthrene by replacing the intermediate CH-groups by N-atoms. Phenanthridine will then form the intermediate step. The relations of phenazone to orthodiazine or pyridazine become evident from its oxidation to pyridazine tetracarboxylic acid by potassium permanganate (p. 584). Tolazone, (C₇H₆)₂N₂, melting at 187°, is prepared from

a, dinitroditolyl (B. 26, 2239).

(B) (a) (C - C - N C - N C - N C - N C (\mu) : I. Metadiazines, or Pyrimidines, are the enalogues of the imidazoles or glyoxalines (p. 496), and, like these, can be viewed as cyclic amidines. Pyrimidines are produced:

z. From smidines of fatty or aromatic carboxylic acids and β -diketones (Pinner, B. **26,** 2125):

$$\begin{array}{c} \textbf{CH_4} \cdot \textbf{CO} \\ \textbf{CH_4} - \textbf{CO}(\textbf{CH_5}) \\ \textbf{Accetylacetone} \end{array} + \begin{array}{c} \textbf{NH_4} - \textbf{CC}_6\textbf{H}_5 \\ \textbf{NII} \\ \textbf{Benzamidine} \end{array} \\ \begin{array}{c} \textbf{CII}_3\textbf{C} == \textbf{N} - \textbf{CC}_6\textbf{H}_5 \\ \textbf{CII} = \textbf{C}(\textbf{CII}_3) - \textbf{N} \\ \textbf{a}, \gamma - \textbf{Dimethyl} - \mu - \text{phenylpyrimidine} \end{array}$$

Similarly, amidines and trimethylene bromide yield tetrahydropyrimidines, while oxypyrimidines result if β -ketonic esters be employed (B. 23, 3820):

$$\begin{array}{c} \text{CH}_{\text{3}}\text{. CO} \\ \text{CH}_{\text{4}}\text{COOR} \end{array} + \begin{array}{c} \text{NH}_{\text{3}}\text{--CCH}_{\text{3}} \\ \text{NH} \end{array} \longrightarrow \begin{array}{c} \text{CH}_{\text{3}}\text{C} \Longrightarrow \text{N} \text{----CCH}_{\text{3}} \\ \text{CH} = \text{C(OH)} \text{--N} \end{array} :$$

and with β -ketone dicarboxylic esters, oxypyrimidine carboxylic esters are produced (compare action of acetmalonic ester upon amidines, B. 23, 161).

2. A rather remarkable formation of the pyrimidines is that due to the polymerization of nitriles (cyan-alkyls) when they are heated to 150° with sodium or sodium alcoholate (1, 267). The cyan-alkines, resulting in this way, are amidopyrimidines, because they change to oxypyrimidines on treatment with nitrous acid, and these are identical with the oxypyrimidines prepared by method of formation (1) (B. 22, R. 327):

The course of the reaction is not yet fully explained. Probably dicyanalkyls are the first products (1, 267).

Cyanalkines are also obtained when sodium or sodium alcoholate acts upon mixtures

of two alkyl cyanides.

 μ, a_1 . Phenyl Dimethyl Pyrimidine, $C_4H(CH_3)_2(C_8H_5)N_2$ (see above), melts at 83° and boils at 276° (B. 25, 2125). $a_1\mu$ -Diethyl- β -methyl Pyrimidine, Cyanconine, $C_4H(C_2H_5)_2(CH_3)N_2$, boiling at 205°, has a narcotic odor and acts similarly to conine (see this). It is prepared from cyanethine by successive conversion into the contraction of the contraction responding oxypyrimidine, chlorpyrimidine, and reduction of the latter (B. 22, R. 328). Consult B. 28, 476, R. 67, for additional alkyl pyrimidines.

Consult B. 28, 476, R. 67, for additional alkyl pyrimidines. μ , a-Dimethyl- γ -amidopyrimidine, Cyanmethine, $C_4H(CH_3)_2(NH_2)N_3$, melting at 180°, and μ , a-diethyl- β -methyl- γ -amidopyrimidine, Cyanmethine, $C_4(C_1)_3$ - $(CH_3)(NH_2)N_2$, melting at 189°, are obtained from methyl and ethyl cyanide, and, like the rest of the cyanalkines, are strongly alkaline bases. Cyanbenzyline, $C_4H(CH_3-C_6H_3)_2(C_6H_5)(NH_2)N_2$, melts at 106° (B. 29, R. 787).

The exphyrimidines possess both a phenol and a basic character. PCl₅ converts them into chlorylyrimidines. Derivatives of the keto- or pyrimidone form are obtained from the exphyrimidines.

oxypyrimidines. They correspond to the three possible formulas:

 μ -Phenyl Oxypyrimidine, μ -Phenyl Pyrimidone, C₄H₂ON₂(C₆H₆), melting at 208° and boiling at 260–263° (30 mm.), results upon heating its carboxylic acid. μ -Phenyl Pyrimidone-carboxylic acid, C₄H₂ON(C₆H₆)(CO₂R), the ester of the preceding acid, melts at 214° and is produced by condensing dicarboxyglutaconic ester with benzamidine or benzamidoxime. Its silver salt and ethyl iodide form γ -ethoxy- μ -phenyl- β carboxylic ester, melting at 59° (B. 30, 1488, 1564).

µ,a-Dimethyl-y-oxypyrimidine, melting at 192°, results from acetoacetic ester and

acetamidine, or when nitrous acid acts upon cyanmethine.

Hydropyrimidines: μ -Phenyl Tetrahydropyrimidine, $CH_2 - CH_2 - NH$ $CH_3 - N = CC_8H_3$ is formed from benzamidine and trimethylene bromide (B. 26, 2122).

Ketotetrakydropyrimidines are obtained from the condensation of diamido-acetone and acid chlorides (B. 25, 1564; B. 27, 277):

CO —CH₂—NH₂

$$CH_2-NH_3$$
CH₂—NH₃
Diamido-acetone

CO —CH₂—NII
$$CH_3-NH_3$$

$$CH_3-N=--$$

$$CH_4-NH_5$$

$$CH_4-NH_5$$

$$CH_4-NH_5$$

$$CH_5-N=--$$

$$CH_5-NH_5$$

$$\mu$$
-Phenyl-\$\theta\$-kettotetraydropyrimidine, mp. p. or \$\theta\$.

The uracil derivatives, which are closely allied to uric acid, are also keto-derivatives of pyrimidine hydrides. Uric acid must be considered as the urelde of isodialuric acid, a diketodioxytetrahydropyrimidine. It represents the naphthalene-like union of CO - NH - C - NH - CO (see the all-NH - CO - C - NH

axasines, B. 28, 1968, and B. 28, R. 909). The cyclic ureides and guanides of the malonic acid series (1, 507; B. 26, 255), the ureide of mesoxalic acid or alloxan, a trihetohexahydropyrimidine (1, 508), etc., belong here.

II. Benzometadiazines: The benzometadiazines or benzopyrimidines are the quinazolines, sometimes called phenmiazines. They are metameric, on the one hand, with the phthalazines and the cinnolines, and, upon the other, with the quinoxalines (p. 594). They may also be viewed as derivatives of the quinolines or isoquinolines by the substitution of an azo-ring:

The simplest quinazoline is not known. Derivatives of it are produced when the acidyl compounds of o-amidobenzaldehyde or of o-amidobenzoketones (pp. 181, 190) are treated with alcoholic ammonia (B. 28, 279):

$$C_8H_4 < \begin{array}{c} CHO \\ NII \cdot COCH_3 \end{array} + NII_3 \longrightarrow \begin{array}{c} CII = N \\ N \cdot \dots \cdot CCH_3 \end{array}$$
o-Acetamidobenzaldehyde

The quinazolines are stable tertiary bases which distil without decomposition. They take up alkyl iodides. Sodium and alcohol reduce them to dihydroquinazolines (B. 26, 1385). Chromic acid in glacial acetic acid oxidizes the quinazolines, in which the CH-group adjacent to the benzene nucleus is free, to ketodihydroquinazolines (or oxyquinazolines, etc.).

a-Methyl Quinazoline, $C_8H_6(CH_3)N_9$, melts at 35° and boils at 238°. a,β -Dimethyl Quinazoline is an oil boiling at 249°. It is formed when ammonia acts upon o-acetamidophenone. a-Phenylquinazoline, $C_8H_5(C_6H_5)N_9$, melting at 101° and boiling above 300°, results when ammonia acts upon o-benzoylamidobenzaldehyde, as well as from o-amidobenzyl-benzamide instead of the expected dihydro-derivative. a-Methyl- β -phenyl Quinazoline, $C_8H_4(CH_3)(C_8H_5)N_9$, melts at 48°. It is obtained from o-acetamido-benzophenone. Chromic acid oxidizes it to β -phenylquinazoline-a-carboxylic acid.

Ketohydroquinazolines and PCl_s yield chlorquinazolines. a and β-Chlorquinazo-

lines, melting at 108° and 96°, are obtained from a- and β -quinazolons. a-Chlor- β -phenyl Quinazoline, melting at 113°, is made from phenyl-a-quinazolon (B. 29, 1310). a,β -Dichlorquinazoline, melting at 115°, is obtained from benzoylene were (p. 592).

Dihydroquinazolines, containing the same atomic grouping, NHCR, as the anhydro-bases of the o-phenylenediamines, the benzimidazoles (p. 499), are to be regarded as the ring homologues of the latter: as anhydro-bases of the o-amidobenzylamines. They result by the elimination of water from the acidyl compounds of o-amidobenzylamine and its substitution products (B. 24, 3096; 25, 3037; 27, R. 74; 29, R. 1131):

$$C_0H_4 < \frac{CH_3 - NH}{NH_4 \cdot COR} \xrightarrow{-H_9O} C_0H_4 < \frac{CH_3 - NH}{N = CR}$$

The reaction proceeds the same if the acidyl-group replaces the aromatic NH₃-residue. Further, the o-amidobenzylacidylamines can rearrange themselves to o-acidylamidobenzylamines (B. 26, 1891, R. 374). The same anhydro-bases may also be obtained by reducing the corresponding o-nitrobenzylamine compounds.

The dihydroquinazolines are rather strong bases, forming stable salts. Free imidehydrogen in them is readily replaced by alkyls. Like the quinazolines, they yield ketodihydroquinazolines upon oxidation. They decompose upon distillation with zinc-dust. Sodium and alcohol reduce them to tetrahydroquinazolines. It may be noted that three isomeric, hydrogenized dihydro-compounds are possible from each c-alkyl quinazoline:

$$\begin{array}{lll} \text{I. } C_6 H_4 < \begin{matrix} \text{CH}_2 - \text{NH} \\ & \mid \\ \text{N}_{-} - \text{CR} \end{matrix}, & \text{II. } C_6 H_4 < \begin{matrix} \text{CH}_2 - \text{N} \\ & \mid \\ \text{NH} - \text{CR} \end{matrix}, & \text{III. } C_6 H_4 < \begin{matrix} \text{CH} = \text{N} \\ & \mid \\ \text{NH} - \text{CHR} \end{matrix}, \end{array}$$

which, probably, adopting the nomenclature of the hydrobenzenes, might be distinguished by the prefixes Δ_1 , Δ_2 , and Δ_3 . Only two isomerides are possible for the dihydroquinazoline itself:

- Δ_1 -Dihydroquinazoline, $C_6H_4 < NH_4 < NH_5$, melting at 127°, results from the reduction of o-nitrobenzyl formamide (B. 24, 3097), as well as by that of a-chlorquinazoline (see above).
- n₁(3)-Phenyl Dihydroquinazoline, C₈H₁(C₆H₅)N₂, melting at 95°, is prepared from o-nitrobenzylformanilide. Under the name of *orexine* it has been recommended as a stomachic.
- a-Methyl Dihydroquinazoline, C₈H₇(CH₃)N₂, is obtained from o-amidohenzylacetamide. β-Phenyl Dihydroquinazoline, melting at 166°, is produced by reducing a chlor-β-phenylquinazoline (B. 29, 1310).

β-Ketodihydroquinazolines, β-quinazolons, are formed, just like the dihydroquinazolines, from the acidyl derivatives of o-amidobenzamide:

$$C_6H_4 < \frac{CO-NH_2}{NH_1 \cdot COCH_3}$$
 or $C_6H_4 < \frac{CO-NH_2}{NH_2 \cdot COCH_3} \longrightarrow C_6H_4 < \frac{CO-NH_2}{N-C_1 \cdot CH_3}$

Analogous products are obtained on heating acidyl derivatives of anthranilic ester with ammonia or with primary amines, or from anthranilic acid and the amides of fatty acids (B. 27, R. 516; 28, R. 783) (p. 213). β -Ketodihydroquinazolines, as mentioned, are produced, in addition to these synthetic methods, by oxidizing quinazolines and dihydroquinazolines.

e-Ketodihydroquinazolines, a-quinazolons, are produced when o-amidobenzaldehydes and -benzene ketones are heated with urea (B. 29, 1300):

$$C_{\text{e}}H_{\text{e}} < \overset{CHO}{\underset{NH_{\text{e}}}{\text{CHO}}} \ + \ \overset{NH_{\text{e}}}{\underset{CO-NH_{\text{e}}}{\text{NH}}} \ \longrightarrow \ C_{\text{e}}H_{\text{e}} < \overset{CH=N}{\underset{NH-CO}{\text{CH}}}$$

The quinazolons possess both feeble phenol and basic characters, hence can also be segarded as oxyquinazolines. They combine with alkyl iodides to n-alkyl derivatives of the keto-form. The isomeric alkoxylquinazolines are obtained from the chlorquinazolines (p. 589).

β-Ketodihydroquinazoline, β-Oxyquinazoline, C₈H₈ON₃, melting at 214°, is produced from anthranilic acid and formamide (J. pr. Ch. [2], 43, 215; 51, 564). Methyl bedide converts it into n-methylketodihydroquinazoline, C₈H₈ON₃. CH₄, melting

71°

a-Methyl-β-ketodihydroquinazoline, melting at 232°, is obtained from o-acetamidobenzamide or o-amidobenzoylacetamide (see above), and also in the oxidation of a-methylquinazoline (B. 28, 279). a-Phenyl-β-ketodihydroquinazoline, C_aH_a(C_a-H_a)NO₃, melting at 236°, is made from phenylquinazoline or o-benzoylamidobenzamide. n-Phenyl-β-ketodihydroquinazoline, melting at 139°, is obtained by oxidizing a-phenyldihydroquinazoline (B. 24, 3055).

a-Ketodihydroquinazoline, a-Quinazolon, is formed from o-amidobenzaldehyde and

e-Ketodihydroquinazoline, a-Quinazolon, is formed from o-amidobenzaldehyde and area, as well as by oxidizing benzylene- ψ -thiurea (p. 177) with Ba(MnO₄)₂. β -Phenyl-e-betodihydroquinazoline, melting at 251°, is prepared from o-amidobenzophenone and

urea (B. 29, 1310).

Tetrahydroquinazolines are produced by the reduction of quinazolines, dihydroquinazolines, and thiotetrahydroquinazolines. They also result in the condensation of o-amidobenzylamines with aldehydes (J. pr. Ch. [2], 53, 414; 55, 356). They may be readily decomposed into benzene ortho-derivatives:

Tetrahydroquinazoline, $C_6H_4 < NH - CH_2$, is amorphous, and results from the interaction of o-amidobenzylamine and formaldehyde. n(3)-Phenyl Tetrahydroquinasoline, $C_6H_6(C_2H_6N)$. $C_6H_6)$, melting at 119°, is derived from o-amidobenzylaniline and formaldehyde, also from phenyldihydro- and phenylthio-tetrahydro-quinazoline (B. 25, 2858). a-Phenyl Tetrahydroquinazoline melts at 100° (B. 25, 3033). See B. 29, 1308, for β -Phenyltetrahydroquinazoline. n-Dibenzoyl- a,β -dimethyl Tetrahydroquinazoline, $C_8H_6(CH_3)_2N_2(COC_6H_6)_3$, melts at 155° (B. 26, 1385).

a-Keto- and thiotetrahydroquinazolines correspond to the cyclic phenylene ureas and -thioureas (p. 502). They are, like these, produced when COCl₂ or CS₂ acts upon o-amidobenzylamines, or by the exit of NH₂ or amine from the urea derivatives of the o-amidobenzylamines (B. 25, 2856; 27, R. 74, etc.):

$$\begin{array}{c} C_{g}H_{4} < \overset{CH_{3}-\mathrm{NHC}_{g}H_{6}}{\mathrm{NH}-\mathrm{CO}} & \text{or} & C_{g}H_{4} < \overset{CH_{3}-\mathrm{NC}_{g}H_{6}}{\mathrm{NH}_{2}} & \longrightarrow C_{g}H_{4} < \overset{CH_{3}-\mathrm{NC}_{g}H_{6}}{\mathrm{NH}_{2}} & \longrightarrow C_{g}H_{4} < \overset{CH_{3}-\mathrm{NC}_{g}H_{6}}{\mathrm{NH}_{2}} & (+ \ \mathrm{NH}_{2}C_{g}H_{6}) \\ & C_{g}H_{4} < \overset{CH_{3}-\mathrm{NHC}_{g}H_{6}}{\mathrm{NH}_{2}} & + \ \mathrm{Cs}_{2} & \longrightarrow C_{g}H_{4} < \overset{CH_{3}-\mathrm{NC}_{g}H_{6}}{\mathrm{NH}_{2}} & \vdots \\ & \mathrm{NH}_{2} & \overset{CH_{3}-\mathrm{NHC}_{g}H_{6}}{\mathrm{NH}_{2}} & \overset{CH_{3}-\mathrm{NC}_{g}H_{6}}{\mathrm{NH}_{2}} & \overset{CH_{3}-\mathrm{NC}_$$

Diketotetrahydroquinazolines are similarly produced from the o-amidobenzamides by means of COCl₂, ClCO₂R, etc., or from urea derivatives of o-amidobenzamide or of the anthranilic acids:

$$C_6H_4 < \frac{CONH_2}{NH_2} + COCl_2 \longrightarrow C_6H_4 < \frac{CO-NH}{NII-CO}$$

Keto- and tetrahydroquinazolines are indifferent bodies. Mention has already been made of their formation from benzometoxazine derivatives, the imido- and thiocoumzones, by heating them with aromatic amines. Oxidants convert them into diketotetrahydroquinazolines, which also result from the oxidation of imido-coumazones (B. 27, 2420). The diketotetrahydroquinazolines possess acid properties and dissolve only in alkalies. PCl, converts them into dichlorquinazolines.

n(3)-Phenyl-a-ketotetrahydroquinazoline, C₈H₇. ON₂. C₈H₈, melts at 189° (B. 27, 74). β-Phenyl a-ketotetrahydroquinazoline, melting at 193°, is obtained from o-amidobenzhydrol and urea, as well as from the corresponding phenylthiotetrahydroquinazoline. The latter is brominated, and the brom-dihydro-phenylquinazoline is then

converted by soda into ketoquinazoline (B. 29, 1307).

a-Thiotetrahydroquinazoline, $C_8H_8SN_9$, melts at 211°. n-Phenyl-a-thiotetrahydroquinazoline, $C_8H_8SN_9$, melts at 260° (B. 27, 2432). β -Phenyl-a-thiotetrahydroquinazoline, melting at 230°, is obtained from o-amidobenzhydrol and

hydrosulphocyanic acid (B. 29, 1305).

Diketotetrahydroquinazoline, Benzoylene Urea, CaH4(C2O2N2H2), melts above 360° and sublimes.

n-Phenyl Diketotetrahydroquinazoline, CaH4(C2O2NHC4H3), melts at 272° (B. 27, 974, 2410, R. 392; compare also B. 30, 1682).

a-Thio β-ketotetrahydroquinazoline, C₂H₄(C₂OSN₂H₂), melting at 284°, is prepared from anthranilic ester and hydrosulphocyanic acid (B. 30, 1098; C. 1897, I, 592).

C. Paradiazine, $\binom{(\gamma)C-N-C(\beta)}{(\delta)C-N-C(a)}$. I. Paradiazines are the pyra-

zines, or piasines, which can be regarded as pyridines, the methine group of which is substituted in the \gamma-position by N. It is almost universally accepted that there is a "para-union" of the two N-atoms in the pyrazines, harmonizing with the formula $N \stackrel{\text{CH}}{=} \stackrel{\text{CH}}{=} \stackrel{\text{CH}}{=} N$ (Wolff, B. 26, 722).

Pyrazines are formed (1) by condensing two molecules of α-amidoaldehydes and a-amidoketones, when an exit of water occurs. Hence they are called aldines or ketines.

Instead of isolating the amido-ketones, the solution of them obtained in the reduction of isonitrosoketones can be distilled with the addition of HgCl2, the oxidizing agent (B. **26**, 1832, 2207):

(2) The synthesis of pyrazines from a-chlor- or bromketo-compounds and ammonia also depends upon the intermediate formation of a amidoketones. Thus, β - bromlevulinic acid and ammonia yield tetramethylpyrazine, with the evolution of carbon dioxide:

Pyrazines occur also in the fermentation products of sugar. Thus, a, y-dimethyl- and trimethyl-pyrazine have been isolated from fusel oil. Pyrazines also result in the action of ammonia upon grape sugar. In this instance the products are pyrazine, methyl- and dimethyl pyrazines (B. 30, 224; J. pr. Ch. [2], 54, 481).

The pyrazines are feeble bases, which give a neutral reaction to litmus. They form readily dissociated salts with acids. Like the pyridines, they form characteristic compounds with metallic salts—e. g., mercuric chloride, auric chloride, etc.

Sodium reduces the pyrazines to piperazines or hexahydropyrazines corresponding to the piperidines. Potassium permanganate oxidizes alkylic pyrazines to pyrazine carboxylic acids, which part with carbon dioxide very readily.

a substance smelling like heliotrope and subliming at the ordinary temperature. It is produced when amidoacetaldehyde or amidoacetal (1, 317) is distilled with a sublimate solution, also by eliminating carbon dioxide from the pyrazine carboxylic acids, and upon

distilling piperazine with zinc-dust (B. 26, R. 441).

Methyl Pyrazine, C₄H₂(CH₃)N₂, boiling at 135°, is obtained from its carboxylic acid (B. 28, R. 551), and constitutes the chief constituent of the bases produced in the action of ammonia upon grape-sugar. a,γ -Dimethyl Pyrazine, Ketine, $C_4H_2(CH_3)_2N_2$, is an oil, boiling at 153°. It is formed in the reduction of isonitrosoacetone, and, together with pyridine bases and other alkylic pyrazines,—e.g., a,γ ,b-methyl diethyl pyrasine, b. p. 179° (B. 24, 4105; 26, R. 442),—upon distilling glycerol with ammonium salts.

a, δ -Dimethyl Pyrazine melts at 48° and boils at 155° (J. pr. Ch. [2], 54, 492). Trimethyl Pyrazine, boiling at 172° , is produced on heating the brom-methylate of a, γ -dimethyl pyrazine (B. 29, R. 980). Tetramethyl Pyrazine, $C_4(CH_3)_4N_3(+3H_2O)$, melts at 86° (75°) and boils at 190° . It is produced when amonia acts upon β-bromleavulinic acid (I, 381), or by reducing β-isonitroso-levulinic acid (B. 25, 1723). a_{γ} -Diphenyl Pyrazine, $C_{\alpha}(C_{\alpha}H_{\alpha})_{\gamma}H_{\gamma}N_{\gamma}$, melting at 196°, results from α-amido-acetophenone, and from n-dibenzyldihydro- a_{γ} -diphenylpyrazine,

 $C_7H_7N < C(C_6H_6) = CH > NC_7H_7$, by the exit of toluene (B. 27, R. 135). The isomeric a, δ -diphenyl pyrazine, melting at 89°, is similarly formed from n-benzyl-dihydro- a, δ -diphenyl pyrazine (see below) by the splitting-off of toluene. a, γ -Diphenyl-dimethyl Pyrazine, $C_4(C_6H_5)_3(CH_3)_2N_3$, melting at 126°, is prepared from isonitrosophenylacetone (B. 29, R. 548).

Tetraphenyl Pyrazine, Tetraphenylaldine, C4(C6H6)4N2, melting at 246°, is made by

reducing the benzil monoximes or dioximes (p. 373) (B. 27, 213).

Pyrazine Monocarboxylic Acid, melting with decomposition at 230°, pyrazine dicarboxylic acid, C₄H₁(COOH)₂N₁(+2H₁O), melting at 256°, and pyrazine tetracarboxylic acid, C₄(COOH)₄N₂, melting at 205°, etc., result upon oxidizing the methylated pyrazines with potassium permanganate. Consult B. 26, R. 442, for other pyrazine carboxylic acids.

Dihydropyrasines, containing two imide groups, are prepared, together with the isomeric indols, in the action of anilines upon a-alkylamidoketone derivatives, RHNC-

H_a. CO—, or from a-bromketones and primary amines.

n-Dibenzene Sulphon-dihydropyrazine, $C_6H_5SO_2N < CH = CH > NSO_2C_6H_5$,

melting at 163°, is obtained from benzene sulphamidoacetal (B. 26, 98). n-Diphenyl-dihydro- a,γ -diphenyl Pyrazine, diphenyldiisoIndol, $C_4H_3(C_6H_5)_2(N\cdot C_6H_5)_2$, melting at 181°, is formed from aniline and phenacyl bromide (p. 248). Different dihydropyrazine derivatives, like n-dibensyl-a,γ-diphenyldihydropyrazine, melting at 163°, n-benzyl-a, b-diphenyldihydropyrazine, etc., are produced by the condensation of benzylamine and phenacyl bromide (B. 27, R. 134).

Dihydropyrazines, with tertiary N-atoms, are obtained from 1,2-diketones and ethylene diamine (B. 22, 346; 26, R. 1009):

$$\begin{array}{c} CH_1-NH_2\\ CH_2-NH_2\\ \end{array} + \begin{array}{c} CO\cdot C_0H_5\\ CO\cdot C_0H_5\\ \end{array} \\ \begin{array}{c} CH_2-N=C\cdot C_0H_5\\ CH_2-N=C\cdot C_0H_5\\ CH_2-N=C\cdot C_0H_5\\ \end{array} \\ \begin{array}{c} CH_2-N=C\cdot C_0H_5\\ CH_2-N=C\cdot C_0H_5$$
 \\ CH_2-N=C\cdot C_0H_5\\ CH_2-N=C\cdot C_0H_5 \\

CH₂—N(C₆H₆)—CH
n-Diphenyl Tetrahydrophenylpyrazine, | , is similarly
CH₂—N(C₆H₆)—CC₄H₆, is similarly
formed from ethylene diphenyl diamine and phenacyl bromide (B. 26, R. 93).

Hexahydropyrazines, piperazines, have already been discussed on p. 314 as cyclic
dialkylene-imides. In addition to the synthetic methods given there, the piperazines are

also prepared by the reduction of the pyrazines with sodium and alcohol (B. 25,724):

µ. Methyl Piperazine, C₄H₉(CH₉)N₃, boils at 155°.

Di. and poly-alkylic piperazines occur each in two stereoisomeric forms: Di-, Tri-,

The cyclic double-acid amides are a,y-diketopiperazines. They have already received consideration (1, 358) after the a-amidocarboxylic acids. Diphenyl Diketopiperazine, diphenyl diacipiperazine, $CH_2 - N(C_8H_5) - CO$ perazine, diphenyl diacipiperazine, $CO - N(C_8H_5) - CH_2$, is formed from anilidocacid acid—see p. 84. Consult B. 25, 2919, 3275, etc., for stereoisomeric diacipiperazine.

a,3-Diketopiperazines are produced in the condensation of oxalic acid with derivatives of ethylene diamine (B. 23, 2028):

$$\begin{array}{c} \text{CH}_2 - \text{NIIC}_6 \text{H}_5 \\ \text{CH}_2 - \text{NIIC}_6 \text{H}_5 \end{array} + \begin{array}{c} \text{COOH} \\ \text{COOH} \end{array} \longrightarrow \begin{array}{c} \text{CH}_2 - \text{N(C}_6 \text{H}_6) - \text{CO} \\ \text{CH}_2 - \text{N(C}_6 \text{H}_5) - \text{CO} \end{array}$$

Chromic acid oxidizes this diketopiperazine to a tetraketopiperazine.

II. Benzoparadiazines: Quinoxalines.—

The quinoxalines, just like the benzimidazoles, are condensation products of o-diamines (p. 95). They result:

I. By the condensation of o-phenylenediamines with glyoxal and 1,2-diketone compounds (Hinsberg, A. 237, 327):

$$C_{6}H_{4} \underset{NII_{2}}{\swarrow} + \underset{COH}{\overset{COH}{\downarrow}} \xrightarrow{-2H_{9}O} C_{6}H_{4} \underset{N=CH}{\overset{N=CH}{\downarrow}} = CH$$

Similarly, benzil yields α, β -diphenylquinoxaline; dioxytartaric acid, α, β -quinoxaline carboxylic acid; etc. The reactions are very complete, even at the ordinary temperatures.

c-Ketone carboxylic acids—e. g., pyroracemic acid and mesoxalic acid—become **expquinoxalines**, while oxalic acid yields dioxyquinoxalines (B. 30, 768):

The o-naphthylenediamines react like the o-phenylenediamines, forming naphtho-quinoxalines. The tetra-amidobenzenes yield benzodiparadiazines.

2. a-Chlorketo-compounds, a-aldehyde alcohols, and a-ketone alcohols—e. g., benzoin, faroin, arabinose, and glucose—condense with o-phenylenediamines. Water and hydrogen are eliminated and quinoxalines remain:

$$C_0H_4 \underset{NH_2}{\swarrow} H_4 \underset{OCCH_3}{\longleftarrow} + \underset{OCCH_3}{\overset{ClCH_3}{\downarrow}} \xrightarrow{\qquad} C_0H_4 \underset{N=CCH_3}{\overset{N=CH}{\searrow}} (H_2O+HCl+H_2);$$

with monoalkylic o-phenylenediamines, on the other hand, the products are dihydroquinoxalines, which ferric chloride oxidizes to azonium bases of the quinoxalines (B. 24, 719, 1875; 25, 1627):

$$C_{g}H_{4} \stackrel{NH_{g}}{\longleftarrow} + OC.C_{g}H_{5} \rightarrow C_{g}H_{4} \stackrel{N}{\longleftarrow} C(C_{g}H_{5}) \rightarrow C_{g}H_$$

The azonium bases are immediately produced by the action of monoalkylic or phenylated o-diamines upon 1,2-diketones (B. 25, 1010; 27, 2355). See also B. 25, 1627.

3. o-Nitrophenyl a-amido-fatty acids, when reduced, yield oxydihydroquinoxalines, which are also obtained from o-phenylenediamines and a-haloid fatty acids (A. 292, 250):

4. o-Phenylenediamines condense with cyanogen to diamido-quinoxalines, which dilute hydrochloric acid changes to dioxyquinoxalines:

$$C_0H_4{<}^{\mathrm{NH}_2}_{\mathrm{NH}_2} + \stackrel{\mathrm{CN}}{\overset{}{\overset{}{\overset{+}}}} \xrightarrow{} C_0H_4{<}^{\mathrm{N} \,=\, \mathrm{CNH}_2}_{\mathrm{N} \,=\, \mathrm{CNH}_2} \xrightarrow{} C_0H_4{<}^{\mathrm{N} \,=\, \mathrm{COH}}_{\mathrm{N} \,=\, \mathrm{COH}}.$$

5. Tetrahydroquinoxalines are produced in the condensation of dioxybenzenes with alkylenediamines:

$$C_0H_4 < OH + H_1N-CH_2 \longrightarrow C_0H_4 < NH-CH_2$$

Behavior: The quinoxalines are feeble monacid bases. Their odor resembles that of quinoline or piperidine. They are readily soluble in alcohol and ether, and more paringly soluble in hot than in cold water. They are stable in the presence of oxidizing spats, while reducing agents convert them into hydroquinoxalines.

Quinoxaline, C₈H₆N₃, is obtained from o-phenylenediamine and glyoxal, by digesting the aqueous solution at 60° with sodium bisulphite. It melts at 27° and boils at 229°.

alkalimetry under the name of lateol (B. 28, R. 628).

Oxyquinoxaline, CaH4[N2C2H(OH)], melting at 265°, is made from its carboxylic acid (see below).

acid (see below).

a.Methyl- β -oxytoluquinoxaline, $CH_2C_2H_2[N_1C_2(CH_2)(OH)$, melting at 220°, and a.Phenyl- β -oxytoluquinoxaline, $CH_2C_2H_2[N_2C_2(C_2H_2)(OH)$, melting at 196°, are prepared from toluylenediamine with pyroracemic acid and phenylglyoxylic acid. They are soluble both in alkalies and in acids. The solutions of the first are colorless, and those of the second yellow in color. a,β -Dioxyquinoxaline, $C_2H_4[N_2C_2H_2O_2]$, from o-phenylenediamine and oxalic acid, or a,β -diamidoquinoxaline (see above) by means of hydrophyric acid is converted by DC_1 into a,β -Dicklorusinoxaline sections with the second property of the second prope chloric acid is converted by PCI₈ into a,β Dichlorquinoxaline, melting at 150°. When the latter is digested with o-phenylenediamine a condensation results, the solutions of which are yellow in color and exhibit an intense yellow green fluorescence. This fact has given it the name fluoflavine, $C_6H_4:(N_4C_9H_9):C_6H_4$, melting at 360°. It loses two hydrogen atoms when it is oxidized, and becomes Quinoxalophenazine, $C_6H_4:$ $(N_4C_2): C_4H_4$ (B. 29, 784):

$$C_{\mathbf{6}}H_{\mathbf{4}} \diagdown \stackrel{N \to \mathrm{CCl}}{N \to \mathrm{CCl}} + \frac{NH_{\mathbf{2}}}{NH_{\mathbf{2}}} + C_{\mathbf{6}}H_{\mathbf{4}} + C_{\mathbf{6}}H_{\mathbf{4}} \swarrow \stackrel{N \to \mathrm{C-NH}}{N \to \mathrm{C-NH}} + C_{\mathbf{6}}H_{\mathbf{4}} + C_{$$

a, il-Dioxynaphthoquinoxaline, Naphthylene Oxamide, C10He(N2C2O2H2) (B. 30, 772).

the latter into quinoxaline dicarbonamic acid, which with bromine and caustic potash

yields a amidoquinoxaline β carboxylic acid, $C_6H_4[N_2C_2(NH_2)(COOH)]$, melting with decomposition at 210° (B. 28, 1657). a Oxyquinoxaline β carboxylic Acid, C₆H₄[N₂C₂(OH)(COOH)], melting at 265° with decomposition, is produced by saponifying the acid ureide produced in the interac-

tion of alloxan and o-phenylenediamine (A. 292, 248).

Hydroquinoxalines. The dihydroquinoxalines are distinguished by their yellowgreen fluorescence:

The fluorescence: $N = CC_6H_5$ Dihydro- a,β -diphenyl Quinoxaline, $C_6H_4 < NH = CHC_6H_5$, melts at 146°, and is

produced in the reduction of diphenylquinoxaline with stannous chloride, or from benzoin and o-phenylenediamine (B. 24, 1870; 27, 2182). n-Methyl Dihydro-a, 3diphenyl Quinoxaline (B. 25, 1632) is oxidized to methylphenostilbazonium hydroxide,

$$C_6H_4 < N = C \cdot C_6H_5$$

 $N = C \cdot C_6H_5$ (see p. 595).

١

n-Methyl-ketodihydro-β-methyl Quinoxaline, n,β-Dimethyl Quinoxalone,

 $C_6H_4 < \frac{N_{--} - CCH_3}{N(CH_3) - CO}$, melts at 78° and boils at 308°. It results from the condense-

tion of methyl-o-phenylenediamines and pyroracemic acid (B. 25, 1630). Tetrahydroquinoxaline, $C_{\kappa} II_{10}N_{2}$, melting at 97° and boiling at 280°, is obtained from pyrocatechol and ethylenediamine (B. 21, 378), or by saponifying its dibensional

phenic derivative, C₆H₄(NSO₅C₆H₅)₈>(CH₈)₈—the reaction-product of ethylene bromide and dibenzene sulphon-o-phenylenediamine (B. 28, R. 756).

e.β-Diphenyl Tetrahydroquinozaline, C₈H₈N₂(C₆H₈), is produced in two isomeric forms, melting at 105° and 142°, when diphenylquinoxaline is reduced with sodium and alcohol (B. 27, 2184).

III. Dibenzoparadiazines: Phenazine Group.—Phenazine is analogous in constitution to anthracene and acridine:







Phenazine.

On the other hand, it is, in its methods of formation and general deportment, very closely related to the dibenzo-derivatives of paroxazine and parathiazine (pp. 581, 583):

Phenoxazine

$$C_{\!e}H_{\!4}\!\!\left<\frac{S}{NH}\right>\!\!C_{\!e}H_{\!4}$$

Dibenzoparathiazine, Thiodiphenylamine

It is the parent substance of an extensive class of dyestuffs, which are to some degree quite important from the technical standpoint—e. g., the eurhodines, toluylene-red, the indulines, safranines, etc., which are in part derived from phenazine itself and partly from higher, condensed paradiazines-e. g., naphthophenazine, naphthazine, etc.

Methods of Formation: I. Phenazines result by the exit of water and hydrogen in the condensation of o-diamines and o-dioxybenzenes:

$$C_{6}H_{4}{<}^{\mathrm{NH}_{9}}_{\mathrm{NH}_{9}} + \frac{\mathrm{OH}}{\mathrm{OH}}{>}C_{6}H_{4} \xrightarrow{} C_{6}H_{4}{<}^{\mathrm{N}}_{N}{>}C_{6}H_{4}.$$

2. Azines are also produced from o-diamines and o-quinones—e. g., β -naphthoquinone, phenanthraquinone, croconic acid, etc. :

$$C_6H_4 \stackrel{NH_2}{\swarrow} + OC_-CH = CH$$
 $OC_-CH = CH$
 $OC_-CH =$

(B. 29, 200). On the other hand, azonium bases result if monosubstituted o-diamines and o-quinones are condensed (see quinoxalines, p. 594):

$$\begin{array}{c} C_{10}H_{6} \swarrow NH_{2} \\ NHC_{6}H_{5} \end{array} + \begin{array}{c} CO-C_{6}H_{4} \\ CO-C_{6}H_{4} \end{array} \longrightarrow \begin{array}{c} C_{10}H_{6} \swarrow N-C-C_{6}H_{4} \\ N-C-C_{6}H_{4} \end{array} \\ \begin{array}{c} O-Amidonaphthyl-phenylamine \end{array} \begin{array}{c} Phenanthra-quinone \\ Phenylnaphthophenanthra-zonium \\ Hydroxide. \end{array}$$

598

Such azonium compounds are also produced by the action of azines and alkyl iodides, and by the deamidation of induline and safranine bases (p. 600).

3. Furthermore, azines result in the oxidation of a mixture of o-diamines and a-naphthol:

$$C_{e}H_{4} <_{\mathrm{NH}_{2}}^{\mathrm{NH}_{2}} + C_{10}H_{7}OH \xrightarrow{\hspace*{1cm}} C_{e}H_{4} <_{N}^{N} > C_{10}H_{4}.$$

4. By the decomposition of o-anilido-(toluido-, etc.)-azo-bodies. Thus, o-anilido-naphthylazobenzene-sulphonic acid, produced by the combination of naphthylphenylamine with diazobenzene-sulphonic acid, breaks down, on boiling with dilute acids, into naphthophenazine and sulphanilic acid:

Behavior: The phenazines are mostly yellow-colored, feebly basic bodies that cannot be distilled without suffering decomposition. They dissolve in concentrated sulphuric acid with a red to blue color. They are again precipitated upon addition of water. They combine with alkyl iodides to azonium iodides (p. 600). They are reduced to

colorless, dihydro-compounds,—e. g., dihydrophenazine, $C_8H_4 < {}_{NH}^{NH} > C_8H_4$,—which are readily re-oxidized to azines.

Phenazine, $C_{11}H_8N_4$, was first obtained from calcium azobenzoate by distillation, and was called Azodiphenylene (p. 587), with which it is isomeric. It may also be prepared from ophenylenediamine and pyrocatechin, and by conducting aniline vapors through a tube

heated to redness, by the deamidation of amidophenazines, and upon boiling formazyl carboxylic ester, CO_2R . CN. $N+C_6H_5$, with concentrated acids (B. 25, 3205); together with various other products in the oxidation of o-amidodiphenylamine,

gether with various other products in the oxidation of o-amidodiphenylamine $C_a\Pi_{4\sim NH}$. $C_b\Pi_{5}$ (B. 26, 383). It melts at 171°.

Ammonium sulphide reduces phenazine to dihydrophenazine. Consult A. 292, 260, for its reduction in acid solutions.

Toluphenazine, CH₃ · C₆H₃ : N₂ : C₆H₄, melting at 117°, is obtained from toluylene-diamine and pyrocatechol; also from o-amidophenyltolylamine and lead oxide (B. 29, 1873).

 a,β -Naphthophenazine, $C_{10}H_6: N_2: C_6H_4$, melting at 142°, is produced, in addition

to the common methods (see above), from naphthylphenylnitrosamine, $C_{10}H_7$, C_6H_5 ,

just as acridine (p. 559) is obtained from formyldiphenylamine. Sym. a,β -naphthazine, $C_{10}II_6:N_2:C_{10}II_6$, melting at 243°, is formed in like manner from β,β -dinaphthylnitrosamine (B. 26, 185). Unsym. a,β -Naphthazine, melting at 283°, was first made by heating nitronaphthalene with lime (naphthase, Laurent, 1840), and was consequently long regarded as azonaphthalene. It was also prepared from a,β -naphthylenediamine and β -naphthylunone. It is most easily made by condensing nitroso- β -naphthylamine and a-naphthylamine (B. 29, 2086). Phenanthrophenazine, $C_{14}H_6:N_2:C_6H_4$, melts at 217° and is obtained from phenanthraquinone and o-phenylenediamine.

The entrance of salt-forming groups, like NH, and OH, converts the phenazines into dyestuffs. In addition to the normal formulas, paraquinoid pseudo-forms come into consideration for these amido- and oxyphenazines (eurhodines and eurhodols) (A. 290, 260):

$$C_{e}H_{4} < \underset{N}{\overset{N}{\underset{\longrightarrow}}} > C_{e}H_{3}NH_{3} \quad \text{or} \quad C_{e}H_{4} < \underset{NH}{\overset{N}{\underset{\longrightarrow}}} > C_{e}H_{3}: NH$$

$$Eurhodine;$$

$$C_{e}H_{4} < \underset{N}{\overset{N}{\underset{\longrightarrow}}} > C_{e}H_{3}: OH \quad \text{or} \quad C_{e}H_{4} < \underset{NH}{\overset{N}{\underset{\longrightarrow}}} > C_{e}H_{5}: O$$

Amido-phenazines: a. Monamido-phenazines, the eurhodines, are produced (1) analogously to the parent substances, from amidated o-diamines and quinones:

$$\begin{array}{c} \mathbf{NH_2.C_cH_2} \\ \mathbf{NH_2.C_{l}H_{2}} \\ \mathbf{NH_2$$

(2) By the action of aromatic monamines upon o-amidoazo-bodies:

$$C_7 H_6 < \frac{N:NC_7 H_7}{NH_2} \ + \ C_{10} H_7 N H_2 \xrightarrow{} C_7 H_6 < \frac{N}{N} > C_{10} H_5 N H_2 (+ C_7 H_7 N H_2 \ + \ H_2).$$

(3) By the condensation of quinone dichlorimides or p-nitroso-dimethyl aniline with amines, in which the p-position is occupied (if this be free, indamines result, p. 174):

$$(CH_3)_2 N \cdot C_6 H_3 <_H^{NO} + \frac{H}{NH_2} > C_{10} H_6 \xrightarrow{\hspace{1cm}} (CH_3)_2 N C_6 H_3 <_N^{N} > C_{10} H_6$$
 Nitrosodimethylaniline \$\beta\$-Naphthylamine Dimethylamidophenonaphthazine

The eurhodines are feeble bases. Their salts are scarlet red in color. They dissolve in concentrated sulphuric acid with a carmine-red color, which, upon the addition of water, passes successively into black, green, and finally red, which is due to the gradual dissociation of polybasic salts, only stable in the presence of concentrated acids. The

ethereal solutions have a yellow-green fluorescence. If they be heated with acids, they become oxyphenazines. They are not applicable technically.

Amidophenazine, C₆H₄(N₂)C₆H₃NH₃, has been prepared from o-diamidophenazine upon heating it with zinc-dust. It results in the oxidation of the diamidodipenylamines, NH₂[2]C₈H₄NHC₈H₄[3]NH₂, or (NH₂)₂[2,4]C₈H₃NHC₈H₅ (B. 29, 1874). It consists of red bronze needles that melt at 265°.

b. Unsym. diamidophenazines are formed in the oxidation of o-diamines (p. 95):

$$C_6H_4 < \frac{NH_9}{NH_2} + C_6H_4 < \frac{NH_2}{NH_2} \xrightarrow{O} C_6H_4 < \frac{N}{N} > C_6H_2 < \frac{NH_2}{NH_2}$$
Unsym. Diamidophenazine.

c. Sym. diamidophenazines, Toluylene-red Group: Symmetrical diamidophenazines are produced when amidated indamines are oxidized (p. 174):

$$NH: C_6H_3 < \frac{NH_2}{N} > C_6H_4NH_2 \xrightarrow{O} NH_2C_6H_3 < \frac{N}{N} > C_6H_3NH_2$$
Sym. o-Amidophenazine.

Instead of using the prepared indamine, a mixture of a p-diamine with a m-diamine may be oxidized, or quinone chlorimides may be allowed to act upon a m-diamine. Thus, tolulyene-red, dimethyldiamidotoluphenazine, NH₂C₂H₅N₂C₆H₃N(CII₃), is produced by oxidizing dimethylparaphenylenediamine with m-toluylenediamine (p. 95). Toluylene-blue appears as an intermediate product (p. 174).

It crystallizes in orange-red needles. It is applied in dyeing under the name Neutral

Red. Its monacid salts are rose-red in color; the diacid, blue; and the triacid, green; the last two are stable only in the presence of strong acids. It colors silk and cotton, mordanted with tannin, a scarlet-red. It yields dimethylmonamidotoluphenazine by dramidation.

ı

Oxyphenazines, eurhodols, are formed (1) when the amidophenazines are heated to 180° with concentrated hydrochloric acid; (2) synthetically, by condensing o-diamines with o-quinones containing hydroxyl. The eurhodols resemble the eurhodines in color and fluorescence.

a-Oxynaphthophenazine, IIOC₈H₄N₂C₈H₄, from amidonaphthophenazine or produced by the condensation of oxy-β-naphthoquinone with o-phenylenediamine, yields two isomeric methyl ethers—an oxygen and a nitrogen ether—corresponding to the two

formulas presented (p. 599) for eurhodol.

Diexyphenazines are obtained similarly to the monoxy-bodies. The condensation of ophenylenediamine with dioxydiketotetrahydronaphthalene (produced by the action of hypochlorous acid upon β naphthoquinone) gives rise to naphthophenazine oxide, $C_6H_4N_4C_{10}H_6$. This is a body resembling ethylene oxide. Hydrochloric acid rearranges it into β -oxynaphthophenazine, $C_6H_4N_2C_{10}H_6OH$, melting at 198° (B. 26, 617; A. 286, 61).

Azonium Compounds: These are important because they are to be regarded as the parent substances of the dyestuffs of the induline, indone, and safranine series, from which they are produced by diazotizing in strongly acid solution, and to which they revert upon treatment with ammonia or alkalies. See p. 597 for their synthetic methods of formation. The phenylazonium salts have been chiefly isolated by means of their ferric chloride double salts. Ethyl Phenazonium Iodide, Methyl Naphthophenazonium Iodide, $C_6H_4(N_2, C_4H_6)C_6H_4$, and $C_{16}H_4(N_2CH_4)C_{19}H_6$, are produced by the union of the corresponding azines and alkyl iodides (B. 30, 391). Phenyl Phenazonium Chloride results from the de-amidation of aposafranine chloride. The ferric chloride double salt, $C_6H_4(N_2C_6H_5, Cl)C_6H_4$, FeCl₂, melts at 186°. Phenyl Naphthophenazonium Chloride, $C_{10}H_6(N_2C_6H_5, Cl)C_6H_4$, is obtained from rosinduline and isorosiduline (p. 601). An isomeric Isophenyl Naphthophenazonium Chloride has been prepared from ψ -rosinduline (p. 601) and also by condensation of β -naphthoquinone with phenyl- α -phenylenediamine (B. 29, 2316, 2967).

Indulines, Indones, and Safranines.—These dyestuffs sustain the same relation to the phenazines as the oxazines and oxazones (p. 580) to phenoxazine, and the thiazines and thiazones to thiodiphenylamine (p. 583). They are quinone-anils, indamines, and indophenols (p. 173), in which the two aromatic nuclei are further linked to each other by the group NR; hence, they are to be considered as meso-alkyl- or alphylderivatives of the paraquinoid forms of the eurhodines and eurhodols (p. 599). However, the induline salts can be converted, by means of their diazo-bodies, through de-amidation, into azonium salts (p. 598), and would therefore have to be viewed as amidated azonium salts; but the corresponding azonium hydrates appear, however, to part readily with water and then pass into the paraquinoid forms (B. 29, 2316, 2752, 2771):

To save space, the paraquinoid formulas for the bases are mostly employed; they will be readily understood from what has been expressed above. The radical (R) may be an alkyl- or an alphyl-group. The

phenylated derivatives primarily are important technically (A. 286, 187; **= B. 28,** 1579).

The indulines are prepared universally (1) by heating p-amidazo-bodies

with monamines in the presence of some mineral acid:

$$NH_3[4]C_6H_4N: NC_6H_5 + C_6H_5NH_3 \longrightarrow NH: C_6H_3 N \longrightarrow N(C_6H_4)$$

The intermediate and by products in this reaction are p-quinone dianil, or azophenine quinone dianil, anilidoquinone dianil, dianilidoquinone dianil, or azophenine Theorem to be considered as the real generators of the includines (B. 25, (p. 173), etc. They are to be considered as the real generators of the includines (B. 25, 2731). Thus, quinone dichlordiimide and phenyl- β -naphthylamine form isorosinduline (B. 29, 2753):

(2) Indulines and indones result from the condensation of oxyquinones and amidoquis with phenylated o-diamines (B. 28, 1714; A. 290, 262):

$$\begin{array}{c} \begin{array}{c} O \\ \text{HO} \end{array} \subset_{\textbf{0}} H_{\textbf{2}} \stackrel{OH}{\longrightarrow} + \stackrel{(C_{\textbf{0}}H_{\textbf{5}})NH}{H_{\textbf{2}}N} \subset_{\textbf{0}} H_{\textbf{4}} & \longrightarrow \\ & H_{\textbf{0}} \\ \end{array} \xrightarrow{O} \subset_{\textbf{0}} H_{\textbf{2}} \stackrel{N(C_{\textbf{0}}H_{\textbf{5}})}{N} \subset_{\textbf{0}} H_{\textbf{4}}; \\ \\ \text{AcNHC}_{\textbf{10}} H_{\textbf{5}} \stackrel{O}{\longrightarrow} + \stackrel{C_{\textbf{0}}H_{\textbf{5}}NH}{H_{\textbf{2}}N} \subset_{\textbf{0}} H_{\textbf{4}} & \longrightarrow \\ \text{AcN: } C_{\textbf{10}} H_{\textbf{5}} \stackrel{N(C_{\textbf{0}}H_{\textbf{5}})}{N} \subset_{\textbf{0}} H_{\textbf{4}}. \end{array}$$

Indones are formed when the indulines are heated with concentrated mineral acids. The indulines are among the longest known aniline dyestuffs (Caro and Dale, 1865; Griess and Martius, 1866). Their constitution has been made more evident by a series of investigations prosecuted in recent years by Fischer and Heppe, Kehrmann, Nietzki, etc. (A. 272, 306; 290, 247; B. 29, 1442, 2318, 2771).
The indulines are classified:

PARTICIPATION OF THE PARTY.

The ms-alkyl derivatives, corresponding to these ms-phenyl-compounds, have also

been prepared in various ways (see B. 30, 394, etc.).

The benzo-indulines and iso rosindulines, on the one side, being derivatives of benzoquinone, and the rosindulines and naphthindulines being derivatives of naphthoquinone, exhibit among themselves great similarity. The first two groups form violet to blue-colored, sparingly soluble salts. Their application in calico printing depends upon their solubility in acetine (1, 475) (acetine print). The ros- and naphth-indulines are strong bases. Their salts have an intense red color, and show red fluorescence. When their strongly acid solutions are diluted a change in color similar to that observed with the safranines occurs. The indulines, like the quinones, readily yield anilido-compounds upon digestion with anilines. Similarly, the indones, when heated with alkalies, become oxyindones. See the safranines for the action of ammonia upon the indulines.

Benzene Induline, Aposafranine, $C_{18}H_{12}N_3$, results by de-amidation of phenosafranine. Further de-amidation yields the phenylphenazonium salt, which regenerates aposafranine by treatment with ammonia. Aposafranine, digested with aniline, forms amilido-aposafranine (B. 28, 1709; 29, 2967). Benzene induline is also obtained from p-amidoszobenzene and aniline. Amidophenyl benzene induline, $NH_3C_6-H_4$, $N:C_6H_3(N_2C_6H_4)$, melting at 150°, is a side-product. By de-amidation it yields phenylbenzene induline. If p-amidoszobenzene be heated with p-phenylene-

nes is produced, and these form *persplaylar*

due of waters annualisate in production, and trace area programpion content dyested (A. 2016, 195).

Since, C_HH_b N_CH_b N_CH_b: NH, from quinone dichlorimide and phosphere, becomes phenylooghthophenessenium (B. 29, 2753) by de-amidsion derivative is obtained from p-nitrosodimethyl smiline with stiline and me. Banko Blue (A. 272, 311) is an amilido derivative of this con-

Resimbaline, NH: C₂H₃·N₄C₄H₄)C₅H₄, melting at 199°, is formed from beases as 0 emphasylamine and smiline, from 0-oxy-a-naphthoquinone-imide and 0-miliophenylamine, as well as from 4-acetamido-o-naphthoquinone and phenyl-o-phenylaminene. ••Rasimaluline, an isomeride, is also produced by the last method. It differs to remindaline in the position of the N. C₆H₅-group with reference to the naphtheless racies. R. 24, 2167; A. 250, 2562.

Rasimaluline and isomeindaline by de-amidation are converted into phenylamido-increasesium satts, which regenerate resimbaline with assessmin. Phenyl Rosinfallist seeks at 235°. Assessmine is its disulphonic acid (D. R. P., 45,370).

Naphthinduline, NH: C₂H₄(N₂C₂H₃)C₃H₄, melts at 250°. It is obtained from leavener-ano-amphthylamine with amphthylamine and amiline (A. 262, 262; 272, 311). Verylatory riselet is its amilido-derivative. A laphthyl Blue is the anilido-derivative of ional amphthinduline; it is produced by the inner condensation of benzene-ano-amphthylamine.

Assimble to $C_{10}H_{1}(N_{1}C_{0}H_{1})C_{0}H_{1}$ of the indones (see A. 286, 242), occars in the form of its sulphonic acid as a poncean-red dyestuff having technical application. Iso-roundone, $C_{10}H_{1}(N_{1}C_{0}H_{1})C_{0}H_{2}$: 0, melting at 224°, is also obtained from nime; benol and phenyl-3-naphthylamine (B. 29, 2755).

Safranines: Safranine salts should be regarded as symmetrical di-: misio-derivatives of the azonium salts, as the unsymmetrical structure termerly proposed for these compounds has been abandoned by all investigators who have been active in this domain of research (B. 29, 1442). They are produced (1) upon oxidizing a mixture of an indoamine and a monamine:

$$\begin{array}{c|c} HN.C_gH_s & H_2N \\ \hline & N + \\ \hline & C_gH_4 \cdot NH_2 \\ \hline & Phenosea France Blue \\ \end{array} \begin{array}{c} O \\ HCI \\ \hline & H_2N \cdot C_gH_3 \cdot NH_2 \\ \hline & Phenosea France Chloride. \\ \end{array}$$

(2) By oxidizing a mixture of m-amido-derivatives of diphenylamine with p-diamines or quinone dichlorimides (B. 28, 1579; 29, 1444):

$$\begin{array}{c} \mathrm{NH_{2}(3)C_{6}H_{4}} \\ + \mathrm{NH_{2}C_{6}H_{6}[4]NHC_{6}H_{5}} \\ + \mathrm{NH_{2}\cdot C_{6}H_{4}[4]NH_{2}} \\ \end{array} \xrightarrow{O} \\ \begin{array}{c} \mathrm{NH_{2}\cdot C_{6}H_{2}} \\ \mathrm{NH_{2}\cdot C_{6}H_{4}} \\ \end{array} \\ \begin{array}{c} \mathrm{N} \\ - \mathrm{NH_{2}\cdot C_{6}H_{5}NH(C_{6}H_{5})} \\ \end{array} \\ \begin{array}{c} \mathrm{N} \\ \mathrm{N}(C_{6}H_{5})Cl \\ \mathrm{Phenomauveine.} \\ \end{array}$$

(3) By the action of ammonia upon the acet-derivatives of certain indulines:

$$\begin{array}{c} \text{AcNHC}_{6}\text{H}_{3} < \frac{N}{N(C_{6}\text{H}_{8})\text{Cl}} > C_{6}\text{H}_{4} \xrightarrow{\text{NH}_{8}} \text{AcNH} \cdot C_{9}\text{H}_{8} < \frac{N}{N(C_{6}\text{H}_{8})\text{Cl}} > C_{8}\text{H}_{4} \cdot \text{NH}_{r} \end{array}$$

The safranines usually form monacid, red-colored salts. The solutions in concentrated sulphuric or hydrochloric acids are green in color. Upon dilution they become the current discount of the current o blue, then red (dissociation of unstable polyatomic salts; compare the eurhodines, p. 1500). The reverse in color-change occurs upon adding acid to the dilute salt solutions. The sparing solubility of their nitrates is noteworthy. The alcoholic solutions usually exhibit a strong yellowish-red fluorescence. Views in regard to the structure of the free bases have been proposed. Reducing agents convert safranines into leuco-compounds, which in the presence of alkalies are rapidly reoxidized by the air to safranines.

The lowest member of the safranines is-

Phenosafranine, C₁₈H₁₅N₄Cl. It consists of leaflets, green in color, or of steel-blue

needles. Baryta separates safranol.

When its monodiazo-compound is boiled with alcohol, aposafranine chloride is produced; the acetyl derivative of the latter, upon treatment with ammonia, again yields an acetyl phenosafranine (B. 30, 1565). Unsym. dimethyl- and diethylphenosafranines (B. 28, 1356) are obtained from dimethyl- and diethyl-p-phenylenediamine with two molecules of aniline. Dimethylphenosafranine is the basis of the dyestuff fuchsia. Giroffit of commerce is an homologue. n-Tetraethylphenosafranine is the violet dyestuff amethyst.

Tolu-safranine, C₁₈H₁₃(CH₃)₂N₄Cl, from toluylenediamine, o-toluidine (1 molecule) and aniline (I molecule), is the chief constituent of common safranine, occurring in commerce as a brown paste or yellow-red powder, employed in cotton and silk dyeing as a substitute for safflor. The necessary base-mixture for its production is obtained from the "aniline oil for safranine." This is partially diazotized and the product

This is partially discounted and the product and the product broken up into paratoluylenediamine and orthotoluidine by reduction.

Naphthophenosafranine Chloride, NII₂C₁₀II₅(N₂C₆II₅. Cl)C₆II₃NII₂. Its acetyl derivative is produced from acetyl rosinduline and ammonia (B. 30, 1566).

The dyestuff indazine, C₆II₅NIIC₆H₃(N₂ClC₆H₅)C₆H₃N(ClI₃)₂, is closely allied to the safranines in its method of formation. It melts at 218°, and is obtained from diphenyl-n-phenylenediamine and nitrosodimethyl aniline. The analogous non-methylated body, from nitroso-aniline and diphenyl-m-phenylenediamine, or from m- and p-amidodiphenylmine, is identical with Phenomauveine, which is closely related to mauveine, the first aniline dye to prove valuable technically (Perkin, 1856). Mauveine is produced by oxidizing aniline containing toluidine with potassium bichromate or lead peroxide. Magdala Red belongs to the safranines (Hofmann, B. 2, 412). It results peroxide. Magdala Red belongs to the safranines (Hotmann, B. 2, 412). It resums from amidoazonaphthalene and a naphthylamine hydrochloride. It probably has the following constitution:

$$\mathrm{NH_{2}C_{10}H_{5}} \stackrel{N}{\overbrace{\underset{N(C_{10}H_{7})Cl}{\overset{N}{\frown}}}} C_{10}H_{5}\mathrm{NH_{2}} \ (\mathrm{B.} \ \ \mathbf{26,} \ \ \mathbf{2235} \ ; \ \ \mathbf{30,} \ \ \mathbf{1567}).$$

Safraninones and Safranols are to be viewed as sym. amido- and oxyderivatives of the indones. Like the safranines, they are prepared from m-oxydiphenylamines with nitrosodimethyl aniline or nitrosophenol (B. 28, 270, 503, 1354, 1578). Safraninone, $C_{19}H_{13}N_{2}O$, and Safranol, $C_{19}H_{12}N_{3}O_{2}$, are made by boiling phenosafranol, $C_{19}H_{12}N_{3}O_{2}$, are made by boiling phenosafranol.

nine with baryta-water or caustic potash (B. 30, 399).

Fluorindenes: Fluorindene is the simplest representative of this class of dyestuffs. It corresponds to triphendioxazine (p. 580):

The fluorindenes result by oxidizing or heating the salts of o-diamines; unsym. diamidophenazines appear as intermediate products (p. 600):

The fluorindenes usually form green-colored crystals, which sublime without decomposition, and are sparingly soluble. Their solutions show a beautiful brick-red fluores-

Methyl Fluorindene, $C_6H_4 = (N_2H) - C_6H_2 - (N_2CH_3) - C_8H_4$, is obtained from the hydrochloride of diamidophenazine and methyl-o-phenylenediamine (B. 28, 395). Phenyl Fluorindene, $C_6H_4N_3HC_6H_2N_2(C_6H_5)C_6H_4$, results from the condensation of aposafranine chloride (p. 601) with o-phenylenediamine (B. 29, 367). Diphenyl Fluorindene, $C_6H_4=(N_1C_6H_5) \oplus C_6H_2 \oplus (N_1C_6H_5) \oplus C_6H_4$, is produced in the oxidation of azophenine, and also from phenylinduline by sublimation (B. 28, 293). Triphenazine Oxazine is a mixed oxazine-phenazine. It is formed from unsymmetric or the condensation of the

dioxyphenazine with o-amidophenol, or from amidophenoxazone with o-phenylenediamine

(B. 28, 299):

$$C_{e}H_{4} \underset{N}{\stackrel{O}{\swarrow}} C_{e}H_{2} \underset{NH_{4}}{\stackrel{O}{\swarrow}} + \underset{NH_{4}}{\stackrel{NH_{5}}{\swarrow}} C_{e}H_{4} \underset{\longrightarrow}{\longrightarrow} C_{e}H_{4} \underset{N}{\stackrel{O}{\swarrow}} C_{e}H_{2} \underset{NH}{\stackrel{N}{\swarrow}} C_{e}H_{4}.$$

4. TRIAZINES.

Derivatives of the three possible metameric triazines are known:

A. Sym. Triazines, Cyanidines: The formula of symmetrical triazine corresponds to the hypothetical Trihydrocyanic Acid, to which the metallo-hydrocyanic acids (1, 231) have been referred. Furthermore, a series of polymeric cyanogen compounds—e.g., cyanuric acid, sulphocyanuric acid, cyanuric chloride, melamine, isomelamine, etc. - are derivatives of this triazine. They have already been discussed.

Alkyl- and phenyl-derivatives of sym. triazine or cyanidine are obtained:

1. By the action of aluminium chloride upon a mixture of benzonitrile and benzoyl chloride or acid chlorides. When benzoyl chloride is used, the reaction (best with the addition of ammonium chloride) proceeds as follows (B. 25, 2263):

$${}_{2C_{6}H_{5}CN+C_{6}H_{5}COCl} \xrightarrow{C_{6}H_{5}CCl} \underset{N-C(C_{6}H_{5})=N}{\overset{OC.C_{6}H_{5}}{\overset{NH_{5}}{\longrightarrow}}} \overset{C_{6}H_{5}C-N}{\underset{N-C(C_{6}H_{5})=N}{\overset{C}{\longrightarrow}}} \overset{C}{\underset{N-C(C_{6}H_{5})=N}{\overset{C}{\longrightarrow}}}$$

2. By the action of anhydrides of the fatty acids upon aromatic carbon-amidines (B. 25, 1624):

$$\begin{array}{c} C_6H_5C - NII_3 \\ \parallel \\ NII + NII_2C(C_6II_5) = NH \end{array} \xrightarrow{O(COCH_3)_2} \begin{array}{c} C_6H_5C - N - CCH_3 \\ \parallel \\ N - C(C_2H_5) = N \end{array} ;$$

carbonyl chloride acts the same as the anhydride of the fatty acid, with the production of oxycyanidines (B. 25, 1424).

The cyanidines are weak, monacid bases. They are more or less readily decomposed into ammonia and carbonic acids.

Diphenyl Methyl Cyanidine, C₃(C₆H₆)₂(CH₂)N₃, melting at 110°, is made from benzamidine and acetic anhydride. It is oxidized to diphenylcyanidine carboxylic acid, which loses water readily and becomes diphenyl cyanidine, C₂(C₂H₅), HN₂, melting at

75° (B. 23, 2382).

Triphenyl Cyanidine, Cyanphenine, C₂(C₂H₅)₂N₃, was first obtained from benzoyl chloride and potassium cyanate (Cloez, 1859), then by the polymerization of benzonitrile with concentrated sulphurio acid; from benzonitrile, benzoyl chloride, and Al₂Cl₆ (see above), as well as by the action of sodium upon a mixture of cyanuric chloride and brombenzene (proof of constitution). Compare B. 29, R. 1124, for the action of sodium upon benzenitrile. Nascent hydrogen decomposes it into ammonia and lophine; compare the similar conversion of Cyanur-triethyl, triethyl cyanidine, into triethyl glyoxaline (B. 28, R. 66). Perchlortrimethyl Cyanidine, C₁(CCl₂)₂N₂, melting at 96°, results from the polymerization of trichloracetonitrile.

Diphenyl Oxycyanidine, $C_3(C_6H_5)_2(OH)N_3$, melting at 289°, from benzenylamidine and COCl₃ (B. 23, 163), forms a well crystallizing sodium salt. PCl₅ converts it

Thane and urea (A. 288, 318).

Diamido-cyanidines are also found in the guanamines, which are produced on heat-Emg guanidine fatty-acid salts or biguanide with fatty acids:

$$\begin{array}{c} NH_{2}C-NH_{2} \\ N-C(NH_{2})=NH \end{array} + \begin{array}{c} NH_{2}C-N-CH \\ \parallel N-C(NH_{2})=N \\ \\ Biguanide \end{array}$$

Piperyl Amido-cyanidine, C₃(NC₅H₁₀)(NH₂)HN₃, melting at 104°, is similarly cobtained by heating piperyl guanide with formic acid, or by treating it with chloroform and caustic potash, even at 0° (B. 25, 525).

Normal cyanuric acid (1, 419) is a trioxycyanidine, cyanuric chloride is a trichlor-cyanidine, melamine is triamidocyanidine, and ammelide and ammeline (1, 427) are cyanidine-and dioxyamidocyanidines. Isocyanuric acid and its derivatives are

To be regarded as derivatives of a triketohexahydrocyanidine.B. Unsym. (a-)-Triazines.—But few derivatives of the simple ring are known: **E,2-Diphenyl-3-oxy-a-triazine**, C₃(C₆H₅)₃(OH)N₃, melting at 218°, is produced in the condensation of benzil with semicarbazide (B. 28, R. 110):

$$\begin{array}{c} C_8H_5.CO \\ C_8H_5.CO \end{array} + \begin{array}{c} H_2N-CO \\ H_2N-NH \end{array} \longrightarrow \begin{array}{c} C_8H_5C = N-C(OH) \\ C_8H_5C = N-N \end{array}$$

n-Phenyl- and n-phenyl-n-alkyl ketotetrahydro-a-triazines are made by heating the unsym. phenylhydrazido-acetic acid ester (p. 127) with formamide and substituted formamides (B. 28, 1228):

$$\begin{array}{c} \text{COOR} + \text{RIINCHO} & \longrightarrow & \text{CO-NR} - \text{--CII} \\ \downarrow & \downarrow & \downarrow & \downarrow \\ \text{CII}_2 - \text{N}(C_6 \text{H}_5) - \text{NI}_2 & \cdots & \downarrow \\ \text{CII}_2 - \text{N}(C_6 \text{H}_5) - \text{N} & \cdots & \cdots \end{array}$$

The derivatives of benzo- or phen-a-triazine are more numerous.

(1) by the reduction of sym. o-nitrophenylacidyl hydrazines:

$$C_{\text{e}}H_{\text{e}} < \stackrel{NO_{\text{g}}}{\underset{NH}{\longrightarrow}} \stackrel{COH}{\longrightarrow} C_{\text{e}}H_{\text{e}} < \stackrel{N}{\underset{N}{\longrightarrow}} \stackrel{CII}{\underset{N}{\longrightarrow}}.$$

(2) By the condensation of formazyl compounds on boiling them with concentrated acids (B. 25, 3206, 3540; 26, 2788):

$$C_6H_5N = N$$
 $C_6H_4NH = N$
 $C_6H_5NH_2$
 $C_6H_5NH_2$
 $C_6H_5NH_2$

The phen-a-triazines are yellow-colored, crystalline compounds, having an alkaloid-like odor. They are very slightly basic.

Phentriazine, C₆H₄(CN₂H), melting at 75° and boiling at 235-240°, results from the reduction of o-nitrophenylformylhydrazine, or by the exit of CO₂ and aniline from formazyl carboxylic ester. Phenmethyl Triazine, C₆H₄[CN₃(CH₃)], melting at 89°

and boiling at 250-255°, is obtained from 0-nitrophenylacetylhydrazine. Phentriasyl Methyl Ketone, $C_0H_0[COSH_0]$, melting at 114°, is derived from formazyl methyl ketone.

The phendihydro-a-triazines are related to the phen-a-triazines. They are obtained, instead of the expected alkylidene amido-derivatives (B. 24, 1002, R. 948), from o-amido azo-compounds and aldehydes:

$$C_{6}II_{4} < \stackrel{\mathrm{NH}_{9}}{\underset{N \,=\, \mathrm{NC}_{4}\mathrm{H}_{5}}{\mathrm{H}_{5}}} + \, \mathrm{CH}_{9}\mathrm{O} \longrightarrow C_{6}\mathrm{H}_{4} < \stackrel{\mathrm{N} \,=\, \mathrm{NC}_{4}\mathrm{H}_{5}}{\underset{N \,=\, \mathrm{NC}_{4}\mathrm{H}_{5}}{\overset{\mathrm{N} \,=\, \mathrm{NC}_{4}\mathrm{H}_{5}}{\mathrm{H}_{5}}}$$

These compounds are colorless. They are feebly basic, stable bodies, which can be

heated with hydrochloric acid to 150° without decomposition.

Tolu-n-tolyl-a-dihydrotriazine, $C_1H_a[CH_1N_3(C_1H_1)]$, melts at 178°. Naphthon,c-diphenyl-a-dihydrotriazine, $C_{10}H_a[CHN_3(C_2H_3)_1]$, melting at 193°, is formed from benzene-azo- β -naphthylamine and benzaldehyde.

C. Phendihydro- β -triazines are derived from adjacent a- or β -Triazine. They are ring homologues of the azimido-benzenes, and are prepared from the o-amidobenzylamines and o-amidobenzamides with nitrous acid, just as the phendihydrometadiazines or dihydroquinazolines are obtained from the carboxylic acids (p. 590):

$$C_{6}H_{4} \underbrace{\stackrel{NH_{2}}{\underset{CH_{2}-NHC_{6}H_{5}}{H_{5}}}} \underbrace{\stackrel{N_{2}O_{2}}{\underset{CH_{2}-N.C_{6}H_{5}}{H_{5}}} C_{6}H_{4} \underbrace{\stackrel{NH_{2}}{\underset{CO-NH}{\underset{N_{2}O_{2}}{NH_{2}}}} C_{6}H_{4} \underbrace{\stackrel{N=N}{\underset{CO-NH}{\underset{N_{2}O_{2}}{NH_{2}}}} C_{6}H_{4} \underbrace{\stackrel{N=N}{\underset{CO-NH}{\underset{N_{2}O_{2}}{NH_{2}}}} C_{6}H_{4} \underbrace{\stackrel{N=N}{\underset{CO-NH}{\underset{N_{2}O_{2}}{NH_{2}}}} C_{6}H_{4} \underbrace{\stackrel{N=N}{\underset{N_{2}O_{2}}{\underset{N_{2}O_{2}}{NH_{2}}}} C_{6}H_{4} \underbrace{\stackrel{N=N}{\underset{N_{2}O_{2}}{NH_{2}}}} C_{6}H_{4} \underbrace{\stackrel{N=N}{\underset{N_{2}O_{2}}{NH_{2}}} C_{6}H_{4} \underbrace{\stackrel{N=N}{\underset{N_{2}O_{2}}}} C_{6}H_{4} \underbrace{\stackrel{N=N}{\underset{N_{2}O_{2}}}} C_{6}H_{4} \underbrace{\stackrel{N=N}{\underset{N_{2}O_{2}}}} C_{6}H_{4} \underbrace{\stackrel{N=N}{\underset{N_{2}O_{2}}}} C_{6}H_{4} \underbrace{\stackrel{N=N}{\underset{N_{2}O_{2}}}} C_{6}H_{4}$$

Phen-n-phenyl Dihydro- β -triazine, $C_aH_a[CH_aN_a(C_aH_a)]$, melts with decomposition at 128° (B. 25, 445).

Phen-n-benzyl Dihydro-3-triazine, CaH₄[CH₂N₃(C₇H₇)], melts at 91° (B. 28, R.

Phenketodihydro & triazine, Bensazimide, Celle[CON3II], melts with decomposition at 212°. It is formed when N₂O₃ acts upon o-amidobenzenylamidoxime (J. pr. Ch. [2], 37, 432; 43, 446; 48, 92; B. 29, 626; R. 785).

5. TETRAZINES.

Only the first two of the three possible metameric tetrazine rings are known in certain derivatives:

A. The osotetrazones are derived from adjacent tetrazine. They result in the oxidation of the osazones, and are to be viewed as n-dialkyl- or dialphyl-dihydro-v-tetrazines:

$$C_6H_5NII-N-CC_6H_5 \longrightarrow C_6H_5N-N=C.C_6H_5$$

$$C_6H_5NII-N-CC_6H_5 \longrightarrow C_6H_5N-N=C.C_6H_5$$

They become triazoles if heated or if acted upon with hydrochloric acid and ferric chloride.

Phen n methyl Dihydrotetrazine, melting at 62°, is a benso-derivative of v-tetrazine. It is formed when nitrous acid acts upon o-amidophenylmethylhydrazine, and corresponds to the phendihydro-3-triazines (J. pr. Ch. [2], 41, 176):

$$C_6\Pi_4$$
 $N\Pi_2$ $N(C\Pi_3)-N\Pi_2$ $+ N_2O_3 \longrightarrow C_6\Pi_4 < N = N \choose N(C\Pi_3)-N\Pi$

The isophendihydrotetracines, on the other hand, are constituted analogously to the

phendihydro-a-triazines. They result by the reduction of the diazo-salts of o-amido-azocompounds (p. 115) (B. 19, 1457; 21, 543):

B. Sym. Tetrazine, $\begin{bmatrix} CH-N=N \\ N-N=CH \end{bmatrix}$, yields several alphyl derivatives, which are characterized by their intense red color, and their stability toward acids, but which are de-

composed by alkalies (B. 26, 2126; 27, 984, 3273):
Diphenyl Tetrazine, C₁(C₆H₆)₂N₄, forms bluish-red leaflets, melting at 192°. It is

easily produced by oxidizing-

Dihydrodiphenyl Tetrazine, consisting of yellow needles. This is produced in the action of excessive hydrazine upon benzimido-ether:

$${}^{2}C_{6}H_{5}C = NH \atop \stackrel{\circ}{OR} + {}^{2}NH_{2}NH_{3} \longrightarrow {}^{C_{6}H_{5}C} = N-N-CC_{6}H_{5}.$$

The dihydro-derivative is converted into tetrazine by heating, by moderated oxidants, and even by the oxygen of the air. It can be regained from the tetrazine by reducing the latter with zinc-dust and glacial acetic acid. If the body be boiled with these reagents, the reduction extends further: ammonia and diphenyl triazole (p. 512) are produced. When dihydrodiphenyl tetrazine is boiled with hydrochloric acid, it forms in

part diphenyloxybiazole (p. 516) and in part it becomes the isomeric—

Isodihydrodiphenyl Tetrazine,

CeH5C—NH—N = C.CeH5,

N——NH

NH

which cannot be oxidized to a tetrazine. n-Derivatives of this body may be synthesized from aromatic hydrazines with chloroform and caustic potash:

$$\begin{array}{c} C_8H_5NH \cdot NH_2 \\ CHCl_1 \end{array} + \begin{array}{c} CHCl_2 \\ H_4N \cdot NHC_4H_5 \end{array} \longrightarrow \begin{array}{c} C_6H_5N - N = CH \\ CH = N - N \cdot C_4H_5 \end{array}$$

n-Diphenyl Isodihydrotetrazine, melting at 180°, is obtained by heating formyl phenylhydrazine (B. 30, 1263). n-Ditolyl Isodihydrotetrazine melts at 185° (B. 23, R. 250).

Urazine, Bishydrazicarbonyl, Diurea, CO NH NH, melting at 270°, is a p-diketohexahydrotetrazine. It is produced when hydrazidicarboxylic ester or hydrazidi-

p-disciplination. It is produced when hydrazidicarboxylic ester or hydrazidicarboxylic ester (S. 1897, 11, 264. Diphenyl Urazine, C₈H₈N—NH—CO
CO—NH—N. C₈H₅
CO—NH—N. C₈H₅
C₈H₈NH. NH. CONH₁, and phenylcarbazidic ester are heated, or when alkalies act upon diphenylcarbazidodicarboxylic ester (B. 21, 2329; A. 263, 282; B. 29, 829). An important of the surface of the su isomeric diphenyl urazine is formed when COCl, acts upon sodium phenylhydrazine (B. 26, R. 20).

6. Substances consisting of polyhetero-atomic six-membered rings, which contain O- and S-members, in addition to nitrogen, are not very numerous. Some are produced in reactions similar to those in which the corresponding five-membered rings are formed.

Just as the five-membered azoximes (p. 515) are prepared from the amidoximes and carboxylic acid chlorides, so their corresponding six-membered ring homologues are prepared from amidoximes and a-chlor-fatty acids (B. 22, 3161; 27, 3353; 28, 1374; 29, 2656):

The five-membered furazanes or azoxazoles (p. 514) have corresponding six-membered azoxazine derivatives. The reduction of disonitrosoacetone dicarboxylic ester peroxide leads to oxyazoxazine dicarboxylic ester:

$$CO_{2}RC-CO-CCO_{2}R \longrightarrow CO_{3}RC-C(OH) = CCO_{3}R$$

$$\downarrow N-O-O-N$$

$$\downarrow N-O-NH$$

from which a series of additional azoxazine compounds has been prepared by rearrangement (B. 26, 999).

The thiodianines or diazthines are homologues of the thio-[b,b₁]-diazoles. An n-phenylthiopentahydrodiazthine, melting at 94°, is formed in the condensation of phenylsulpho-carbazinic acid with ethylene bromide (B. 27, 2516):

Benzo-derivatives of the diauthines are produced when the phenylthiosemicarbazides are treated with hydrochloric acid (B. 27, 861) (p. 128):

$$C_6H_4$$
 $NH-NH$
 $NSCNH_2$

Phenylthiosemicarbazide

 C_6H_4
 $NH-N$
 $S-CH$

Benzodiazthine.

Benzodiazthine, *Phenylsulphocarbizine*, melting at 129°, is decomposed by fusion with caustic potash into o amidothiophenol. Benzo-n-methyldiazthine, from unsymmetrical phenyl-methyl semicarbazide, and others behave similarly.

The thialdines (1, 203) contain a six-membered ring, with two S-members and one N-member. They are produced by the action of ammonia, etc., upon the trithicaldehydes.



INDEX.

ABIETIC acid, 334
Acenaphtenone, 410
Acenaphthene, 48, 409, 410
quinone, 410
Acenaphthylene, 410
Acetacetyl pyridine, 535
quinoline, 549
aldehyde-phenylhydrazine, 113
amidine, 129
amido-azobenzene, 115
cinnamic acid, 276
cinnam-lactimide, 276
hydrazobenzene, 118
naphthol, 401
phenetol, 154
triphenyl methane, 352
amino-naphthol ethyl ether, 401
anilide, 82, 18 9
coumaric acid, 280
Acetenyl benzene, 268
hydrindene carboxylic ester, 387
iodosobenzoic acid, 210
nitrotoluide, 501
Acetoacetanilide, 84
acetic ester, 464
phenyl-hydrazine, 127
amido-mandelic acid, 252
phenyl-acetic acid, 214
benzoic acid, 238
anhydride, 198
benzoyl benzoic acid, 350
butyric acid, 46
isatinic acid, 258
methyl pyrone, 522
carboxylic acid, 522
Acetone, 55
oxalester oxime, 494
phenyl hydrazone, 467
methyl hydrazone, 466
nicotinic acid, 536
Acetonyl acetone, 447
methylisoxazolyl ketone, 494, 495
oxindol, 214
oxybenzalacetophenone, 463
Aceto-oxycoumarone, 463

```
Aceto oxyphthalide, 237
phenone, 69, 176, 189, 257, 271, 407
                 acetoacetic ester, 262
                 acetone, 250
                 alcohol, 248
                 anil, 189
                 anilide, 249
                 carboxylic acid, 238, 265
                 chloride, 189
                 homologues, 189
                 orthoethers, 189
                 oxalic ester, 484
                phenylhydrazone, 189
                substitution products, 190
                sulphonic acid, 191.
      phenon-oxime, 189
                      carboxylic anhydride,
                         580
      phenylhydrazone, 481
      phthalaldehydic acid, 237
      piperone, 221
      pyrocatechol, 221
salicylic acid, 224
      thienone, 455
      trimethylene carboxylic acid, 23
      veratron, 221
Acetparatoluidine, 68
    phenylhydrazide, 125
toluides, 75
vanillon, 221
Acetyl acetophenone, 250
       amidobenzophenone, 347
       amidrazone, 130
       anisol, 221
       anthranilic acid, 212
       aurines, 361
       benzene, 189
       benzenylamidoxime. 208
       bornylamine, 326
carbanilide, 86
       carbazole, 477
       carbostyril, 549
diketo hydrindene, 388
       dioxindol, 252
       diphenylene oxide, 476
        durene, 190
```

010	BA.
Acetylene benzenes, 268	Alcohols of triphenyl methane, 361
dicarboxylic ester, 484	Aldehyde, 441, 442
phenetol, 271	acids, 236
Acetyl-fenchylamine, 326	alcohols, 233
hexahydro-cresol, 315	collidine, 528, 532
hydrazobenzenes, 117	green, 358, 547
indols, 466	phenylhydrazones, 466
isatin, 258, 472	Aldehydes, 182, 407
isindazole, 493	of triphenylmethane, 361
isocapronic acid, 329	Aldehydines, 96, 500
mesitylene, 190	Aldehydo benzoic acid, 238
methyl indazole, 492	cinnamic acid, 286
isindazole, 493	dicarboxylic acids, 245
pentamethylene, 26	isophthalic acid, 245
penthiophene, 525	phenoxyacetic acid, 218, 463
tolimidazole, 501	phenylhydroxylamine, 187
opianic acid, 238	nitrobenzaldoxime, 187
oxybenzalacetophenone, 464	Aldehydrazones, 122
phenyl carbaminate, 91	Aldol aniline, 79
phenylene diamine, 500	Alicyclic nucleus, 410
phenyl isindazole, 347, 493	saturated compounds, 18
methyl triazole, 512	unsaturated compounds, 18
urea, 86	Aliphatic substitution products, 61
piperidine, 540	Alizarin, 159, 420, 426, 427, 433
pyrazole, 481	amide, 428
pyrrol, 458	blue, 427, 554
quinoline, 549	green, 554
toluene, 190	bordeaux, 429
trimethylene, 22	brown, 428, 429
xylene, 190	green, 554
Acicular oxylepidene, 381	indigo-blue, 554
Acid esters, 146	orange, 427
fuchsine, 357	yellow, 349
green, 355	Alkali blue, 359
yellow, 115, 138	Alkaloids, 561
Acidum cinnamylicum, 274	Alkines, 412
Acidylated benzenes, 189	Alkoxypyrazoles, 487
Acridic acid, 550	Alkylalphylsulphones, 139
Acridine group, 559	benzaldoximes, 444
Acridone 313 335 347 560	benzenes, 50
Acridone, 213, 225, 347, 560	benzoic acids, 194
Acrolein phenylhydrazone, 485 Acrylaldehydophenoxyl acetic acid, 272	camphor, 331
Acrylic ester, 486	coumarins, 281 cyan-camphor, 331
Addition-reaction, 43	dithiocarbamic acids, 73
Adipic acid, 296, 393	Alkylen-dianilines, 79
Adipin ketone, 26	Alkylic anilines, 470
Æsculetin, 283, 463	anthracenes, 422
Æsculetinic acid, 283	derivatives of anthracene dihy-
Æsculin, 283, 431	dride, 424
Æsculus hippocastanum, 431	diphenyls, 335
Alanine, 87	hydranthanols, 425
Albumen, 253	indols, 467
Albuminates, 466	rhodamines, 366
Alcohol carboxylic acids, 27, 233	rosanilines, 358, 357
derivatives of dibenzyl, 371	Alkylidene anilines, 79
of stilbene, 375	thioureas, 440
Alcohols, 32, 407	ureas, 440
of the naphthalene series, 407	Alkylisoquinolines, 244
	, , , , , , , , , , , , , , , , , , , ,

611

INDEX.

Amido-benzaldehyde oxime, 187

ydrazones, 467 reas, 85
, 482 458 namic acid, 275
amic acid, 275 acid, 274, 276
dibromide, 256 dibromide methyl ester,
256 dichloride, 256
none, 273 ethyl pentoxazoline, 580 iazsulpholes, 518
imethylmethylene ether, 270 de, 498
, 268 acetic ester, 260, 287 -urea, 580
55 , 269
i7 oil, 429
269 1ydrazine, 122 , 533
chine, 269 chol methylene ether, 270
270 .32
432 id, 196
d, 196 : acid, 252
/lamines, 70 197, 499
83
, 202 ıalaldehydic acid, 236
henone, 190, 249
cid, 170 ene, 423
quinone, 425 , 423 ine, 489
zene, 108, 109, 115 sulphonic acids, 137
hthalenes, 398
lene, 115 lehyde, 187 acet derivatives, 187
hetero-ring forma- tions of, 187

```
benzene sulphonic acids, 137
benzhydrol, 344
benzidine, 338
benzoic acid, 211, 214
             lactam, 212
benzophenone, 347
               oxime, 347
benzo-thiazole, 508
benzoxazole, 504
benzoyl formic acid, 258
                     lactam, 471
         glyoxylic acid, 261
benzyl alcohol, 180
       aniline, 181
       chloride hydrochloride,
          180
       methyl ketone, 466
butyl phenyl ether, 146
camphor, 330
chlorstyrene, 465
chlorstyrolene, 268
cinnamic acid, 276
compounds, 31, 70
coumaric acid, 282
derivatives, 351, 405
desoxybenzoin, 466
diimido-phenol, 172
dimethyl aniline, 95
         phene, 179
dinitro phenol, 154
diphenyl, 336
           amine, 95, 118
diphenylene ketone, 419
             methanes, 343
ditolyl, 336
ethyl benzene, 77
      indene, 386
furfurane, 448
hemipinic acid, 242
hexabydrobenzoic acid, 300
          phenylacetic acid, 300
hexamethylene, 295
hydratropic acid, 214, 252
hydrindene, 387, 388
hydrindone, 387
hydrocarbostyril, 215
      cinnamic acid, 214, 255
isophthalic acid, 242
  propyl benzene, 77
         indene, 386
lutidine, 533
         dicarboxylic acid, 538
mandelic acid, 78, 251
                lactam, 251
lactam, 471 methyl benzenes, 75
       indene, 385, 386
       oxazoline, 503
```

012 INDEX.	
A i 3 shl shiorolo anthornio actor	Amido etruolena efer
Amido-methyl thiazole carboxylic ester,	Amido-styrolene, 267
506	terebenthene, 326
triazole, 512	tertiary butyl benzene, 77
naphthalenes, 396	tetramethyl diamido-triphenyl m
naphthoic acid, 408	thane, 358
naphthols, 401	tetraoxybenzene, 166
naphthol sulphonic acids, 403	tetrazole, 520
naphthoquinone, 405	tetrazotic acid, 520
imide, 407	thiazole, 505
nicotinic acid, 536	carboxylic acid, 506
nitro-hydrocinnamic acid, 214	thiazolines, 506
phenyl-acetic acid, 214	thiophene, 455
octyl benzene, 77	phenol, 157
oxazoline, 503	phenols, condensation of, 157
oxindol, 214, 471	trimethylphene, 179
oxybiphenyls, 340	piperidenes, 540
hydrindene, 387	pyrazole, 483
naphthoic acid, 409	triphenyl carbinols, 354
pentamethyl benzene, 76	methane, 352
phenanthrenes, 414	Amidrazones, 125, 129, 205
phenazines, 599	[Aminobenzene], 74
phenol, 70, 152, 503	[Aminophene], 74
phenols, 152	Ammon-chelidonic acid, 537
condensation of, 153	Ammonium hydroxides, 77
phenol sulphonic acid, 156	Amygdalic acid, 430
phenthiazine, 584	Amygdalin, 430
phenyl acetic acid, 214	Amygdonitriloglycoside, 430
aceto lactam, 471	Amyl anthracene, 423
acetylene, 268	Andropogon nardus, 321
alanine, 253	Anethol, 259, 268, 269, 282
hydrochloride, 254	Anethum fæniculum, 269
amido-acridine, 560	graveolens, 271
benzene induline, 601	Angrecum fragans, 280
fatty acids, 214	Anhydrides of diazophenols, 479, 516
glyceric acid, 255	Anhydroacetophenone benzil, 381
guanidine, 128	bases, 96, 401, 480, 507
lactic acid, 253	bis-amido benzophenone, 347
methane, 95	bisketo hydrindene, 388
methyl pyrazolon, 488	ecgonine, 570
quinoline, 546	formaldehyde-aniline, 79
osotriazole carboxylic acid,	geraniol, 309
509	hippuric phenyl ester, 200
propiolic acid, 285	oxyvinyl benzoic acid, 286
sulphides, 158	benzoic acid anhydrid
toluoxazole, 504	286
thiazole, 507	benzoic acid imide, 28
phthalic acids, 241	sulphamine-benzoic acid, 216
phthalide, 236	Anil-acetoacetic ester, 84
polymethyl benzenes, 76	biguanide, 128
propiophenone, 249	guanidine, 128
propyl benzene, 77	Anilic acid, 240
indene, 386	Anilides of fatty acids, 81
pyrazoles, 483	Anilido-acetic acid, 84
pyridines, 533	phenyl hydrazide, I
quinoline iodmethylate, 547	amido-naphthol ethers, 402
quinolines, 547	aposafranine, 601
quinones, 547 quinone, 170	benzimidazoline, 502
quinoxaline-carboxylic acid, 596	benzothiazole, 508
sulphonic acids, 399	benzorazole, 504
surprionic acids, 399	nemovemie! 2nd

ido-butylidene aniline, 79 crotonic ester, 84 dicarboxylic acids, 91 dimethyl pyrrol, 124 methyl thiazoline, 507 naphthoquinone, 405 anil, 407 oxynaphthoquinone, 405 phenitidine, 154 phenyl carbamic ethyl ether, 86 isoquinoline, 556 thiobiazoline, 517 phosphoric dichloride, 80 propionic acid, 84 pyrrols, 124, 458 thiobiazole, 479, 517 diazole, 518 line, 66, 74, 391, 466 black, 75 blue, 79, 35**9** haloids, 91 oil, 76 potassium, 73 salts, 75 lines, 70 1-pyroracemic acid, 84 succinmide, 129 uvitonic acid, 84, 549 saldoxime, 218 se oil, 269 sic acid, 145, 225, 269 aldehyde, 219 sidine, 152 sil, 375 silic acid, 369, 375 soin, 372 sol, 145, 1**46** solines, 366 syl alcohol, 217 nidalin, 144 ol, 269 hracene, 48, 384, 422 blue, 429 brown, 429 carboxylic acids, 424 derivatives, 421 dibydride, 424 disulphonic acid, 423 ethyl nitrate, 423 group, 420 hexahydride, 424 mono-sulphonic acid, 423 oil, 49 perhydride, 424 sulphonic acids, 423 thrachrysone, 429 thraflavic acid, 428 thragallol, 428 thramine, 423

Anthranil, 212, 256 carbonic acid, 212 Anthranilic acid, 211 Anthranol, 424 Anthra-purpurin, 428 pyridine quinone, 561 pyridines, 561 quinolines, 554 quinone, 423, 424, 425 carboxylic acids, 429 disulphonic acid, 426 mono-sulphonic acid, 426 quinoline, 554 Anthrarobin, 424 Anthrarufin, 424, 428 Anthrol, 423 Anthroxanaldehyde, 250, 256 Anthroxanic acid, 259 Antibenzaldoxime-methyl ether, 185 febrine, 75, 82 phenylglyoxylic acid oxime, 258 pyrine, 75, 120, 121, 443, 480, 488 Apiol, 268, 270 Apione, 166 Apionol, 166, 271 Apoatropine, 567 camphoric acid, 332 cinchene, 573 codeine, 576 morphine, 576 phyllenic acid, 537 quinene, 573 safranine, 601 Arbutin, 429 Arbutus uva ursi, 429 Archil, 162 Arecaidine, 565 Arecaine, 565 Arecoline, 565 Aristol, 144 Arnica Montana, 163 Aromatic acid amides, 199 amido-ketones, hetero-ring formations of the, 190 monocarboxylic acids, 21 I compounds, 30 derivatives, 20 hexacarboxylic acid, 246 monocarboxylic acids, 191 monoketones, 188 nitrolic acids, 208 pentacarboxylic acids, 246 polyalcohols, 247 substitution products, 61 tetracarboxylic acids, 246 Arsenanilido-dibromide, 81 dichloride, 81 Arsenobenzene, 132

014 INI	OEX.
Arsenphenylamines, 81	Azosulphime anilides, 517
	sulphimes, 441, 479, 480, 517
Artemisia Barellieri, 319	toluenes TTS
cina, 315	toluenes, 113
Artificial camphor, 323	trimethyl benzenes, 113
isocinnamic acid, 275	Azoxazine derivatives, 442
musk, 57, 68	Azoximes, 441, 479, 480, 515
Asafætida, 160, 283	Azoxyaniline, 112
Asarone, 268, 270	benzene, 70, 111, 155
Asaronic acid, 231	benzide, III
Asarum europæum, 270	benzoic acids, 215
Aseptol, 156	compounds, 111, 112
Asparagine, 253	derivatives, 63
Aspartic acid, 253	Azoxylenes, 113
Asperula essence, 281	toluene, 112
Asperula odorata, 281	Azuline, 361
Atroglyceric acid, 255	Azulmic acid, 446
lactinic acid, 252	Azylines, 116
Atropic acid, 278	
Atropine, 253, 498, 567	
Atroxindol, 214	
Auramine, 348	В.
Aurantia, 93	
Aurine, 143, 361	BADEN acid, 399
Aurines, 351, 359, 360	Baldrianic camphor, 324
Azimethylene, 445	Balsams, 334
group, 445	Basler blue, 602
Azimide benzenes, 510	Bay-oil, 270
Azimides, 96, 441, 480	Benzal acetoacetic ester, 287
Azimidobenzene, 97, 511	acetone, 272
benzoic acid, 214	amido sulphonic acid, 186
Azimidol, 122	angelic lactone, 288
Azines, 397, 579	aniline, 185
Azobenzene, 112, 113	azine, 185
azoresorcinol, 161	tetrabromide, 185
monocarboxylic acid, 215	benzamidine, 204
benzide, 113	bromide, 184
benzil, 373	butyric acid, 278
benzoic acid, 215	chloride, 184
black, 400	Benzaldehyde, 66, 69, 176, 183
camphenone, 330	condensations, 449
camphor, 330	substitution products, 186
carmine, 602	sulphonic acid, 188
compounds, 112, 487	diacetal ester, 184
of naphthalene, 397	diethyl acetoacetic ester, 288
derivatives, 31	ether, 184
diphenylene, 337, 598	diketohydrindene, 388
dyes, 114	dimethyl ether, 184
imido compounds, 63	diphenylmaleId, 377
Azoles, 478, 479	doxime-o-acetic acid, 186
Azonaphthalene, 397	carboxylic acid, 236
naphthols, 401, 406	anhydride, 230,
Azonium compounds, 600	580
Azoopianic acid, 238, 242	ether, 439, 440
phenine, 173	Benzaldoximes, 185
phenols, 155, 173	ethylamine, 185
phenylene, 215	glutaric acid, 289
phenylmethane, 113	lævoxime, 288
rubin, 400	lævulinic acid, 255, 288, 391
styrolene, 267	malonic acid, 288
	• • • • • • • • • • • • • • • • • • • •

Benzalmalonic acid ethyl ester, 288
half-nitrile of, 288
mesityl oxide, 273
phenylhydrazone, 185
phthalide, 376
propionic acid, 278
pyrazolon, 487
Benzamerone, 383
amide, 199, 206
bromide, 203
chloride, 203
haloids, 209
iodide, 203
sulphonic acid, 216
amidine, 204
diazo-benzene, 204
hetero-ring formations, 205
phenyl-thiurea, 204
urethane, 205
amidoxime, 204
anilide, 199
imide chloride, 203
Benzantialdoxime acetate, 186
Benzaurin, 360
Benzazimide, 213, 606
Benzeines, 359, 360
Benzene, 18, 30, 45, 47, 437
azocarbonamide, 127
dimethyl aniline, 115
diphenylamine, 115
ethane, 113
methane, 112, 113
naphthalene, 397
naphthyl-phenylamine, 398
nitroethane, 114
phenol, 155
resorcinol, 161
sulphonic acid, 103
derivatives, 30
diazoacetanilide, 109
anilide, 108
carbonamide, 103
carboxylic acids, 114
sulphones, 103
azthine, 128 carboxylic acid, 239, 242, 243
carboxylic acid, 239, 242, 243
sulphonic acids, 136
sulphoxide, 139
halogen substitution products, 57
hexabromide, 293
carboxylic acid, 43
hydrazophenetol, 155
hydrocarbons containing a single
nucleus, 47
induline, 601
of crystallization, 351
oxyquinones, 170 pentacarboxylic acid, 246
phenolphthalide, 363

```
Benzene phthalin, 361
         pyrogallolphthalide, 363
         ring, decomposition of, 44
               formation, 450
               formations, 41
         resorcinol phthalide, 363
         sulphamide, 135
         sulphinic acid, 139
         sulpho-diazobenzene amide, 135
         sulphone, 140
         sulphonhydrazide, 135
         sulphonic acid, 69, 135
         sulphonitramide, 135
         tetracarboxylic acid, 246
         theory, Kekulé, 30
         thiosulphonic acid, 139
         tricarboxylic acid, 191, 245
         sulphonic acid, 136
Benzenylamidine, 204
amido-thio-phenol, 199
         amidoxime, 208
                      acetic acid, 608
                            anhydride, 442
                      butyric acid, 208
                      ethyl ether, 208
                      glycollic acid anhy-
                         dride, 208
                      methyl ether, 208
         azoxime-thiocarbinol, 515
         bromoxime-acetic acid, 208
         carbonyl azoxime, 515
         chloroxime acetic acid, 208
         compounds, 203
         dioxytetra-azotic acid, 205
         diphenyldiureide, 204
         ethyl ether, 208
         fluoroxime acetic acid, 208
         hydrazidine, 204, 205
           drazoxime ethidene, 208
           droxylamine-acetic acid, 208
         methoxime bromide, 208
         nitroxime-acetic acid, 208
         oximido-carbonic ester, 208
                 glycollic acid, 208
         tetrazotic acid, 205, 519
         trichloride, 208
Benzglycocyamidine, 213
     hydrazoin, 117, 185, 445
     hydrol carboxylic acids, 349
            ether, 344
            lactone carboxylic acid, 349
     hydrols, 344
        droxamic acid, 206, 207
                       ethyl ether, 207
                  methyl ether, 207
            imic acid chloride, 208
        drylamine, 344
           amine, 344
benzoic acid, 349
lactone, 349
```

11.2	
Benzhydrylhydroxylamine, 349	Benzometadiazines, 589
Benzidam, 74	methyldiazthine, 608
Benzidine, 337	orthoxazinon, 580
disulphate, 337	morpholine, 581
dyes, 138, 338	nitrile, 69, 83, 202
rearrangement, 79, 118	paradiazines, 594
sulphonic acid, 339	phenol, 142
Benzil, 373	phenone, 345, 367
carboxylic acid, 376	bromide, 345
dianil, 374	carboxylic acids, 349
dicarboxylic acid, 376	chloride, 345
dioxime diacetates, 374	dicarboxylic acid, 350
dioximes, 373	dilactone, 3t
Benzilic acid, 369	phenones, 344
Benzilmonanil, 374	phenone sulphide, 526
monoximes, 373	synthesis, 345
Benzilo-tropeine, 568	phenonoxime, 346
Benzimidazole, 497, 500	pyrazolon, 493
hydrides, 501	pyrone, 523
azoles, 499, 501	pyrrodiazole, 510
azolines, 501	pyrrol, 462
imidazolon, 502	quinone, 167, 299
imido-ethyl ether, 204	Benzorthodiazines, 586
imidothio-ethyl ether, 204	oxazinon, 580
isothiazole, 181, 479, 507	oxazole, 504
isoxazole group, 495	azoles, 153, 503
Benzoazimidole, 511	oxyazo benzene, 172
bisimidazoles, 501	Benzoylacetaldehyde, 250
methylimidazole, 501	aldoxime, 250
diazthine, 608	acetic acid, 259
furfurane, 463, 464	ester, 259
hydrometoxazine anil, 581	acetoacetic ester, 261
thiazine anil, 583	acetone, 250, 481
thiometoxazine, 581	acetonitrile, 260, 494
thiazine, 583	phenone monoxime, 494
methyldifurfurane dicarboxylic es-	acetyl, 250
ter, 464 ph e nyl metoxazine, 580	acrylic acid, 288 amido-cinnamic acid, 276, 277
pyrazolons, 493	cinnam-lactimide, 276
pyrrol, 463	anthranilic acid, 212
furazane, 515	azide, 20I
furfurane, 462, 463	azimide, 198
glyoxalines, 499	benzhydroxamic ester, 207
Benzoic acid, 69, 176, 193, 464	benzoic acid, 395
thionyl hydrazone, 216	benzylamine, 200
trichloride, 208	bromide, 198, 199
anhydride, 198	butane, 189
sulphinide, 216	butylcarbinol, 249
Benzoîn, 372, 502	carbinol, 190, 248, 255
anilanilide, 373	acetate, 248
anilide, 373	benzoate, 248
indulines, 601	chloride, 248
hydrazone, 372	oxime, 249
oxime, 470	chloride, 198, 257, 467
resin, 274	chlorimide, 199
toluide, 373	conine, 564
Benzoisothiazole, 507	coumarone, 379, 463, 464
keto morpholine, 581	crotonic acid, 288 cyanacetic ethyl ester, 263
leinic acid, 300	clemenonia criili cercil mo?

	D 1 - 1 - 1 - 1 0
coylcyanacetic methyl ester, 263	Benzpinacone dicarboxylic acid, 378
acetoester-carboxylic acid,	pyrrol, 465
265	sulph-hydroxamic acid, 135
cyanide, 257	terephthalic acid, 349
oxime, 258	thiazoles, 157, 507
diazobenzene, II4, 20I	thiophene, 269, 462, 463, 465
ketohydrindene, 388	trichloride, 208
methyl aniline, 347	furfurane, 464
oxybenzene, 349	methyl metoxazine, 580
sulphide, 199	trifurfurane tricarboxylic
enguanidine, 213	ester, 464
urea, 213, 592	Benzylacetamide, 180
fluoride, 198	acetate, 178
formaldehyde, 249	acetoacetic acid, 385
formic acid, 257	ester, 260
formoin, 381, 495	acetone, 190, 291, 385
formoxime, 249	acetophenone, 379
formoximic acid chloride, 258	succinic ester, 263
glycocoll, 200	alcohol, 176
collic acid, 198, 200, 261	carboxylic acid, 234
oxylic acid, 261	phenyl ketone, 372
	sulphonic acid, 181
hydrazine, 200 iodide, 198	
	amine, 179, 252
isatin, 258	carboxylic acid, 235
isatinic acid, 258	angelic lactone, 287
isonitroso-acetic ester, 261	aniline, 179
succinic ester, 263	arabinoside, 177
malonic ester, 263	benzene, 342
mesitylene, 345	group, 342
nitride, 198, 201	benzoic acid, 349
peroxide, 184, 198	ester, 198
phenacyl-acetic acid, 381	benzyl-oxyindol, 469
phenol, 348	carbinol, 177
phenyl-alanine, 253	chloramine, 179
hydrazimethylene, 445	chloride, 177
hydrazine, 201	chlormalonic ester, 262
hydrazone-glyoxylic ester,	cyanide, 203
261	desoxybenzoin, 379
phthalic acid, 350	dimethyl carbinol, 177
piperidine, 540	sulphine iodide, 178
propane, 189	diphenyldihydropyrazine, 593
propionaldehyde, 250	diphenyls, 350
propionic acid, 255, 261	disulphide, 178
pyrazole, 481	durene, 343
pyroracemic acid, 261	Benzylene-thio-urea, 583
ethyl ester, 261	ethyl ether, 177
sulphide, 199	ketone, 190
tetrahydroisoquinoline, 557	glutaconic ester, 289
quinoline, 258, 551	glycollic acid, 253
methylene, 190	hydride, 183
toluides, 199	hydroxylamines, 180
tricarballylic acids, 264	hyposulphurous acid, 178
methylene, 190, 260	idene acetone, 272
carboxylic acid, 260	acetophenone, 379
tropine, 569	aniline, 185
xylene, 345	bisdesoxybenzoln, 383
uphenylhydrazide-imide-chloride, 203	derivatives, 487
pinacolines, 378	desoxybenzoln, 379
	diacetophenone, 383
pinacone, 378	mucerohaenone, 202
11—52	

018	DEX.
D. Jilan diskandisansia said see	. Disharal age
Benzylidene diphenylitaconic acid, 382	Biphenol, 339
hydrazine, 185	Biphenyl, 335
imide, 184	carboxylic acids, 340
methyl isoxazolons, 495	dicarboxylic acids, 340
nitroacetophenone, 475	sulphonic acid, 339
phenylenediamine, 185	methylolid, 340
phthalide, 376	sulphonic acid, 339
isophthalic acid, 349	Bipyrocatechine, 339
lævulinic acid, 261	Biresorcinol, 339
malon-carboxylic acid, 265	Bisacenaphthylidene, 410
malonic acid, 262	acetyl glyoxyllic ester phenyl hydra
mesitylene, 343,	zone, 339
methoxime chloride, 208	azobenzil, 373
methylcarbinol, 177	benzimidazoles, 501
ether, 177	benzothiazole, 508
ketone, 190	diketohydrindene, 388
nitramine, 179	dimethylazimethylene, 486
morpholine, 581	glyoxalidine, 499
mustard oil, 180	glyoxaline, 497
oxethylamine, 179	hydrazibenzil, 373
oxyvaleric acid, 255	carbonyl, 607
lactone, 255	isoxazoles, 494
pentaethyl benzene, 343	Bismarck brown, 95, 116
phenol, 343	methylbenzoyl carbinol, 248
phenyl ether, 177	isoxazole, 494
methyl-pyrazolon, 488	muth triphenyl, 133
oxethylamine, 503	nitro-benzyl hydroxylamine, 180
phosphates, 178	phenylalkyl carbamate, 161
phthalazone, 376, 587	methylpyrazolon, 487, 48
phthalimide, 241	pyrazoles, 481
imidine, 376	pyrazolon, 487
succinic acid, 262	tetrazole, 520
anhydride, 262	triazoles, 513
sulphide, 178	Bitter almond oil, 183
sulphone, 178	green, 354, 355
sulphonic acid, 178	principles, 432
sulphoxide, 178	Bordeaux dyes, 403
sulphydrate, 178	Borneo camphor, 324
tartronic acid, 262	Borneol, 324
thiourea, 180	acetyl ester, 325
toluenes, 343	methyl ether, 325
urea, 180	Bornylamine, 326
xylene, 343	chloride, 325
Berberine, 578	Brasilein, 433
Berberonic acid, 537	Brasilin, 433
Bergamot oil, 310	Briganum hirtum, 145
Bergapten, 286	Brilliant green, 355
Betaine, 439, 440, 446	yellow, 370
Betel-phenol, 270	Bromacetanilide, 84, 474
Bidesyl, 381	acetophenone, 190, 248
Bidiphenylene ethane, 418	anilic acid, 170
ethylene, 418	anilido-indone, 386
Bieberich scarlet, 138, 402, 434	aniline sulphonic acid, 137
Bifluorene, 418	benzaldehyde, 186
Biguanide, 128	benzenes, 59
Bihydroisothujol, 314	benzoic acid, 209
quinone, 339	benzophenone, 346
Bilberry, 301	oxime, 346
Bindschedler's green, 174	benzoyl formic acid, 258

ombenzyl alcohol, 180
bromide, 180
camphoric acid, 332
camphoro-anhydridic acid chlorides,
• •
333
chlormethylene homophthalic acid,
393
cinnamic acid, 275, 276
coumarin, 281, 463
cyclohexane, 294
diphenacylens, 380
nhand see
phenyl, 336 ethylbenzamide, 503
ethylbenzamide, 503
naphthalene, 410
hydratropic acid, 252, 253
hydrocinnamic acid, 254
romide of phthalaldehydic acid, 237
indene, 385
isodehydracetic acid, 451
phthalic acid, 242
lævulinic acid, 466
mandelic acid, 251
naphthalenes, 395
naphthoquinone, 404, 405
nitro dinhanul 226
nitro-diphenyl, 336
hydrindone, 387
nitrosobenzene, 70
oxycinnamic acid, 463
hydrindene, 387
indone, 386
pentamethyl benzene, 63
phenanthrene, 414
phenol, 149
phenylhydrazine, 120
phthalide, 236
piperonal, 220
propylpiperidine, 540
pseudocumene, 63
pyrazole, 483
pyridine, 533
pyromucic acid, 451
quinolines, 547
resacetophenone, 249
salicylic acid, 225
styrene, 271
styrolene, 267
thiophene, 454
toluene, 62
xylene, 63
ronner's acid, 399
rucine, 575
illow's reaction, 125
utallylcarbindimethylamine, 461
utenyl trioxybenzene methyl methylene
ether, 270
utyl benzenes, 56
benzoic ester, 198
naphthalene, 394
phenylketone, 189

```
Butyrolactam, 438, 462, 480
      lactone, 437
      phenone, 189
                carboxylic acid, 238
Butyrylacetophenone, 250
       fenchylamine, 326
Buzylene, 131
          compounds, 131
          derivatives, 64
                    Ċ.
CAFFEIC acid, 282
Cajeput oil, 315
Calcium formate, 465
isoferulate, 269
         quinate, 301
Camphan group, 321
Camphanic acid, 332
Camphel alcohol, 325
         amine, 326, 328
Camphelylisocyanate, 328
Camphene, 308, 321
dibromide, 321
            glycol, 325
hydrochloride, 321
Camphenilan, 322
              aldehyde, 322
Camphenilanic acid, 322
Camphenilol acid, 322
Camphenilon, 322
Camphenone, 330
Campho acid, 322, 332
Camphol, 324
           actone, 332
          alcohol, 325
          amide, 328
          amine, 326, 328
Campholene, 329
              dibromide, 329
Campholenic acid, 328
Campholic acid, 328
Campholide, 332
imidine, 332
Camphopyro acid, 332
Camphor, 25, 290, 308, 321, 326, 327
Camphoranic acid, 333
         carboxylic acid, 330
         constitution of, 327
         dichloride, 328
         dioximes, 329
Camphoric acid, 27, 331
                 diamide, 331
                 dichloride, 331
                 imide, 331
                 methyl imide, 331
                        isoimide, 331
            anbydride, 331
```

Comphasimine 208	Carbostyril formation, 277
Camphorimine, 328	
methylene carboxylic acid, 330	styrilic acid, 212
nitrilo acid, 331	styril methyl ether, 548
Camphoro-anhydridic acid, 333	Carboxyethylanthranilamide, 212
onic acid, 333	Carboxyl-apocamphoric acid, 322, 332
oxime, 328	derivatives of the oxytriphenyl
phorone, 26, 331	carbinols, 363
pinacone, 326	of triphenyl carbinol,
quinone, 322, 329	362
semicarbazone, 328	of triphenylmethane,
Camphoryl hydroxylamine, 331	361
malonic ester, 333	Carboxylic acids, 27, 379, 381, 419, 445
Camphylamine, 326	of dibenzyl group, 375
isoazolon, 496	of furfurane, 450
phenylpyrazolon carboxylic ester,	Carminic acid, 405, 433
493	Carone, 319
Cantharene, 294, 432	Caronic acid, 319
Cantharic acid, 432	anhydride, 319
Cantharidin, 432	Carthamin, 433
Cantharinic acid, 432	Carthamus tinctorium, 433
Caoutchouc, 307, 334	Carvacrol, 144, 145, 298
Carbanile, 89, 106	Carvacrotin aldehyde, 219
Carbanilic acid, 85	Carvacrotinic acid, 226
Carbanilide, 85	· ·
	Carvenone 310
Carbazole, 336, 462, 463, 477	Carvenone, 319
blue, 477	Carveol, 319
potassium, 477	methyl ether, 317
Carbazotic acid, 150	Carvestrene, 312
Carbinol benzoic acid, 233, 251	Carvol, 145
bromide benzoic acid, 235	Carvomenthene, 293, 313
Carbinols, 353	menthylamine, 317
Carbobenzoyl acetic acid, 265	Carvone, 299, 320
propionic acid, 265	tanacetone, 319
lactone, 265	Carvoxime, 321
benzyl malonic acid, 265	Carvum carvi, 145
cinchomeronic acid, 537	Carylamine, 317
cyclic compounds, 17, 18	Castoreum, 142
diphenylimide, 90, 502	Catechin, 228, 232
ethoxy phenylmethylpyrazolons, 484	Catechinic acid, 232
hydrocinnamic acid, 393	Catechu-tannin, 232
Carbolic acid, 142, 143	Caucasian petroleum, 291
mandelic acid, 264	Central formula, 40
methoxy-phenylmethylpyrazolons,	Cetraria vulpina, 382
484	Cetyl benzene, 57
Carbonic acid, 441, 442	Cetyldesoxybenzoin, 371
ethidene ester, 478	Cevadine, 575
Carbon-oil acid, 143	Chavibetol, 268, 270
Carbonyl amidophenol, 153, 504	Chavica betle, 269
amidothiophenol, 157	Chavicol, 268, 269
benzenyl azoxime, 208	Chelidamic acid, 537
oxime anhydrides, 442	Chelidonic acid, 522
pyrrol, 458	Chloracetoacetic ester, 464
thiocarbanilide, 446	acetone, 466
phenylglyoxylic acid, 265	
pyridyl glyceric acid, 536	aceto-phenone, 190, 248 acridine, 560
pyrotritartaric acid, 451	aldehyde, 504
pyrrol gloxylic acid, 460	anil, 169, 464
styril, 288, 548	anilamic acid, 170
carboxylic acid, 187, 288	l amide, 170

621

	~·· · · · · · · · ·
iloranilic acid, 170	Chlorphenyl isoquinoline, 556
anilido-indone, 386	mustard oil, 508
aniline, 92	paraconic acid, 263, 391
benzaldehyde, 186	quinazoline, 590
benzene hexachloride, 293	phthalazine, 586
benzenes, 58	propyl benzene, 177
benzoic acid, 209	pyridine, 26, 533
phenone oxime, 346	quinazolines, 590
thiazole, 508	oline, 547, 556
trichloride, 224	
	quinone, 45
bromstilbene, 375	salicyl chloride, 224
camphor, 328	salicylic acid, 225
carbazole, 477	stilbene dibromide, 375
carbonylphenyl-ortho-phosphoric acid	dichloride, 375
dichloride, 224	styrene, 271
carbostyril, 285	styrolene, 267
cinnamic acid, 62, 275, 276	thiazole, 505
desoxybenzoln, 379	thiophene, 454
dibrom-hydrindone-carboxylic acid,	toluene, 62
388	toluic acid, 235
diphenyl, 336	triazoles, 512
ethyl benzene, 177	Chromotrope, 403
hydratropic acid, 252, 253	Chrysamine, 338
hydrocinnamic acid, 255	ammic acid, 428
hlorination, exhaustive, 43	aniline, 356, 560
done carboxylic acid, 393	anisic acid, 214
isonitrosoacetophenone, 258	arobin, 428
phthalic acid, 242	azin, 428
lutidine dicarboxylic acid, 538	azine, 424
methyl benzamide, 234, 236	azol, 423
benzanilide, 234	Chrysene, 48, 416
benzoic acid, 234, 236	fluorene, 388, 417
benzonitrile, 234	alcohols, 419
benzoyl chloride, 234	Chrysenic acid, 408, 416
methylene camphor, 330	Chrysin, 523
glyoxaline, 497, 498	Chrysofluorene, 418
isoquinoline, 556	Idine, 116
trichlorimidazole, 501	ketone, 416, 419
naphthalenes, 395	phanic acid, 428
naphthalene sulphonic acids, 399	phenine, 370
naphthols, 391	quinone, 416
naphthoquinone, 404, 405	Cicuta virosa, 56, 283
nicotinic acid, 536	Cinchene, 573
nitrocamphor, 328	Cinchomeronic acid, 536
hydrindone, 387	Cinchona bark, 301
nitrosobenzene, 70	Cinchonine, 256, 572
lorobenzil, 375	Cinchoninic acid, 549
benzylacetophenone, 379	Cinene, 311
Hor-o-diketo penta-methylenes, 26	Cineol, 315
alorophyl, 434	Cineolic acid, 315
	Cinnamcarboxylic acid, 392
oxydiphen oxazone, 582	Cinnamenyl acetone, 273
phenyl quinoxaline, 596	oxime, 273
hydrindene, 387	acrylic acid, 285
indone, 386	angelic acid, 285
naphthoquinone, 405	
phenanthridine, 558	crotonic acid, 285
phenol, 149	cyanacrylic acid, 289
phenyl benzoyl hydrazine, 201	malonic acid, 289
hydrazine, 120	Cinnamic acid, 254, 266, 274

1.1.2.1.1	
Cinnamic acid, amide, 275	Common camphor, 327
anhydride, 275	Condensation, aromatic, 43
anilide, 275	Condensations of o-diamines, 95
	Condensed nuclei, 29, 384
chloride, 275	
derivatives, 275	Congo yellow, 338
dibromide, 256	Coniferine, 272, 430
ethyl ester, 256	Coniferyl alcohol, 272, 430
methyl ester,	Conine, 541, 562
256	hydrochloride, 564
dichloride, 256	tartrate, 564
ethyl ester, 275	Constitution of benzene nucleus, 39
methyl ester, 275	Convolvulin, 431
nitrile, 275	Convolvulus orizabensis, 431
phenyl ester, 275	purga, 431
aldehyde, 272	Conylene urethane, 564
cyanhydrin, 256	Conyrine, 532
Cinnamon oil, 272	Coriander oil, 310
Cinnamyl alcohol, 266, 271	Coriandrol, 310
aldehyde, 266	Cotarnic acid, 242
cyanhydrin, 287	Coto bark, 287, 349
amine benzylidene acetone, 383	Cotoin, 349
carboxylic acid, 286, 287	Coumalic acid, 522
cyanide, 287	Coumalin, 522
formic acid, 287	Coumaran, 464
idene-acetophenone, 383	Coumarates, 279
methyl ketone, 272	Coumaric acid, 277, 279, 280, 282
pyrrols, 460	dimethyl ether, 279, 280
tolimidazole, 501	Coumarilie acid, 281, 463, 464
Cinnolines, 586	Coumarin, 281, 285
Cis-benzene hexachloride, 293	bromide, 281
Citraconanil, 91	homologues, 281
Citraconanilic acid, 90	monomethyl ester acid, 281
Citrazinic acid, 529, 538	propionic acid, 289
Citrel, 310	Coumarinic acid dimethyl ether, 279
Citrene, 311	dimethyl ester, 281
Citronellal, 310	Coumarins, 279, 523
nellic acid, 310	Coumarone, 442, 462, 463, 464, 465
nellol, 309	Coumaroxime, 281
Citrus aurantium, 311	Creolin, 144
bergamia risso, 286	Cresol, 143, 144, 160
decumana, 432	benzeine, 360
Coal tar, 48	Cresolin, 144
Cocaine, 274, 569	Cresorcin, 161, 162
Coccinic acid, 434	Cresotinic acid, 47, 225, 251
Coccus cacti coccinelliferi, 433	chloride, 224
Cochenillic acid, 434	Crocein acid, 403
Codeine, 576	Croconic acid, 27, 97, 171
Coerulein, 366	hydride, 171
Coerulignone, 339	Crotonic acid, 165
Coffee bean, 301	Crotonylene, 57
Coke, 48	Crystal violet, 357, 358
Collidine, 532	base, 358
dicarboxylic acid, 537	Crystallin, 74
Colophonium, 291	Crystalline veratrine, 575
Colophony, 322, 334	Cubebine, 272
Copellidine, 540	Cubebs, 272
Comanic acid, 522	Cumaric aldehyde, 272
Comazonic acids, 580	Cumarone, 269, 271
Comenic acid, 523	Cumarones, 168
J-J	

	Cyanpyrrol, 458
acid, 278	toluenes, 202
•	toluic acid, 244 .
, 184	triphenylmethane, 362
43	Cyanur-triethyl, 604
	Cyclic alkylenimides, 435
5	urea derivatives, 85
•	alkylidene-ureas, 446
369	amidines, 96
	ammonium salts, 137
050	anhydrides of oxy-acids, 442
ie, 273	carbonyl-ureas, 446
<i>ium</i> , 56 ohol, 177	derivatives of dibasic carboxylic acids, 435
ine, 179	diazides, 137
2	double-acid amide, 252, 253
9	esters of amido-acids, 435
sulphide, 518	of oxy-acids, 435
433	ethers, 441, 442
fora, 433	of the glycols, 435
	of the thioglycols, 435
30	guanidines, 96
ne, 238, 260, 263	ketones, 26
carboxylic acid, 265	sulphureas, 97
÷, 130	thiocarbonyl thioureas, 446
:	ureas, 96, 439, 441
wide as as	Cyclobenzoquinone, 299
oride, 237, 238	diolefines, 18
de, 238	diphenyltetrazolium chloride carbox-
, 349 id, 236, 241, 242, 243	ylic ester, 521 formazylcarboxylic ester, 339
ester, 24I	heptadiëne, 28
loride, 241	heptane, 28
tic ester, 245	heptanon, 28
shol, 234, 235	heptene, 28
ine, 235	hexadiën, 294
oride, 234, 235	hexadienes, 293
nide, 244	hexandion, 296
588	hexane, 48, 291
331	diol, 294
cid, 287, 288	triol, 295
ethyl ester, 288	hexanhexene, 295
methyl ester, 288	hexanol, 294, 296
288	carboxylic acid, 301 hexanon, 296, 301
nethane, 349	hexanon, 290, 301
8	hexantriones, 297
1	hexenes, 293
amic ester, 245	olefines, 18
p, 442	paraffins, 17, 18
Ĭ.	pentadiene, 25
id, 331	pentan acetic acid, 27
;88	carboxylic acid, 27
-camphor, 330	dicarboxylic acid, 27
nes, 409	pentanon, 26
100 005 Fo.4	tetracarboxylic acid, 27
102, 205, 504	2,3-dion-1,4-dicarboxylic es-
drazine, 130	ter, 28
thyl triazole, 512:	pentane, 25

624 I	NDEX.
Customentanol 26	Diacetylisodurene, 233
Cyclopentanol, 26	lutidine, 535
pentanon, 26	mesitylene, 233
pentene, 25	Diagonal formula, 40
propane, 22	Dialphylsulphoureas, 73
triolefines, 18	Diamido-anthracene, 423
Cymene, 53, 56, 144, 326	
Cymophenol, 145	azo-benzene, 115, 116
thiophenol, 145	benzenes, 94
Cytisine, 565	benzidine, 338
	benzoic acids, 214
	benzo-methylimidazole, 501
	phenone, 348
D.	biphenyl dicarboxylic acid, 341
 -	disulphonic acid, 339
DAHLIA, 358	cyanidine, 605
Dahl's acid, 399	dimethyl aniline, 97
Dambonite, 295	diphenyl, 338
Dambose, 295	dinaphthyls, 410
Daphne alpina, 431	dioxyquinone, 166, 170
mesereum, bark of, 283	diphenic acid, 340
Daphnetic acid, 283	diphenyl, 337
Daphnetin, 283, 463	ene oxide, 476
Daphnin, 283, 431	methane, 343
Decahydrocarbostyril, 552	phthalides, 363
naphthalene, 413	sulphide, 158
quinoline, 545, 551	ditolyl sulphide, 158
Decompositions of the naphthalene ring	
392	hydrazobenzene, 117
Dehydracetcarboxylic acid, 522	hydromellitic tetraethyl esters,
dracetic acid, 522	246
drofichtelite, 416	hydroquinone, 164
mucic acid, 451	mesitylene, 95, 232
thiotoluidine, 158, 507	naphthalenes, 397
Dermatol, 230	phenazine, 96, 599
Desaurines, 371	phenols, 154
Desoxyanisoin, 371	phenyl-tolyl, 338
benzoin, 371	pseudocumene, 95
carboxylic acid, 376	pyrazole, 483
toluoin, 371	quinone-imide, 154, 172
Desylacetic acid, 377	stilbene, 370
acetophenone, 380	tetraoxybenzene, 166
anilide, 373	thiodiphenylamine, 584
bromide, 373	toluenes, 95
Determination of position of benzene sul	
stitution products, 34	methane, 352
of positions, 36	Diamidrazone, 130
Dextromandelic acid, 251	Diamines, 94
tropic acid, 253	Dianilidoquinone, 168, 170, 173
Diacetanilide, 82	anil, 168, 170, 173
benzidine, 337	dianil, 168, 170, 173
caffeïc acid, 283	toluquinone, 170
Diacetonyl-dibenzyl, 377	Dianisidine, 340
osotriazone, 124	Dianthranol, 424
phenolphthalein, 364	Dianthryl, 424
phenylhydrazide, 126	Diatropic acid, 278
phenylhydrazone, 123	Diazides, 153
Diacetylbenzene, 233	Diazines, 584
cyanbenzyl-cyanide, 244	Diazoacetic ester, 99, 445, 484, 486
durene, 233	alkali salts, 101

	i.
liazoamidobenzene, 108	Diazotoluene acid, 99
benzoic acid, 215	Diazthine derivatives, 442
bodies, 63, 73	Diazthines, 608
compounds, 78, 106	Dibenzal diphenyldihydrotetrazone, 131
toluenes, 109	Dibenzamide, 199
benzene acid, 98, 102	Dibenzamidine urea, 205
amidobrombenzene, 109	Dibenzene sulphodihydropyrazine, 539
toluene, 107	sulphone methylenephenylene
anhydride, 102	diamine, 501
anilide, 108	sulphonhydroxylamine, 135
chloride, 99, 102, 125	I)ibenzenylazo-sulphime, 517
cyanide, 103	azoxime, 374, 515
diazo-resorcinol, 161	hydrazidine, 205
ethylamine, 109	isazoxime, 516
imide, III	Dibenzhydroxamic acid, 207
methyl ether, 102	Dibenzofurfurane, 462, 476
nitrate, 102	Dibenzolacetylmethane, 379
perbromide, 70, 102	paradiazines, 597
piperidine, 109	pentene, 388
potassium, 102	pyrones, 523
sulphocyanide, 102	pyrrol, 462, 477
sulphonic acid, 103	thiophene, 158, 462, 476
acid anhydrides,	Dibenzoyl, 373
137	acetic acid, 380
acids, 137	acetone, 379
sulphoxide, 125	acid, 255
sulphoxyl, 100	benzenes, 350
thiophenyl ester, 157	diamidoethylene, 497
benzenes, 99	dibenzyl, 381
benzoic acids, 215	dimethyl-tetrahydroquinazo-
compounds, 63, 73, 99, 100	line, 591
of naphthalene, 397	ethane, 380
cyanides, 114	ethyl ester, 255
derivatives, 78.	furazane, 515
hydrazo-compounds, 131	glyoxime, 381
imido-benzoic acid, 215	hydrazine, 201
compounds, 110	malonitrile, 379
methane, 70, 145, 439, 440, 445, 486	methane, 379
disulphonic acid, 445	methyl ester, 255
naphthalene sulphonic acid, 400	phenolphthalein, 364
naphthalic acid, 397	phenyl ethane, 380
naphthionic, 400	propionic acid, 381
azonium salts, IOI, IO2	styrene, 381
oxides, 441, 480, 516	stilbene, 381
oxyamido benzene, 70	succinic acid, 382
compounds, 110	Dibenzyl, 369
perbromides, 105	acetic acid, 379
perhalides, 102	amine, 178
phenolcarboxylic acid, 155	adine-triacetophenones, 383
cyanide, 155	benzenes, 350
phenois, 154	carbinol, 378
phenylene diamine, 116	carboxylic acid, 376
propionic ester, 445	cyanurate, 180
pseudo-cumene acid, 99	dicarboxylic acid, 376, 377
selenide, 441	diphenol methane, 378
succinic ester, 445	diphenyldihydropyrazine, 593
sulphides, 441, 517	ethane, 380
tetrazole, 520	ethylamine, 380
thiazole hydrate, 505	glycollic acid, 380
11-53	••
**	

Dibenzyl guanidine, 180	Dichlordihydroterephthalic acid, 304
homologues, 370	diketohydrindene, 388
hydrazine, 180	diphenyl, 336
hydroxylamine, 180	ethyl benzene, 247
idene acetone, 383	hydrindene, 387
phenylene diamine, 185	hydrocinnamic acid, 256
	quinone dicarboxylic ester,
succinic acid, 382	
ketone, 378	. 305
malonic acid, 379	quinone disulphonic scid,
methane, 378	164
monocarboxylic acid, 376	indigo, 475
nitrosamine, 179	indol, 468
oxalate, 178	indone, 386, 393
piperazine, 594	isoquinoline, 244, 556
pyridine, 532	maleinimide anil, 91
succinic ester, 260	methoxyphthalic acid anhydride
urea, 180	241
chloride, 180	methylchlorvinyl-o-diketone, 46
Dibromacetophenone, 249	methylene phthalide, 286
aniline, 92	naphthalenes, 395
anthranilic acid, 68, 213	naphthoquinone, 386, 393, 406
anthraquinone, 425	nitroscetophenone, 249
benzophenone, 346	ethyl benzoyl formic ack
chlor-hydrindone carboxylic acid,	393
393	salicyl chloride, 224
cinnamic acid, 275, 385	stilbene, 370
cyclohexane, 295	oxyindene carboxylic acid, 386, 39
diazophenol sulphonic acid, 155	phenol, 149
diphen y l, 336	phenyl paraconic acid, 263
diphenylene oxide, 476	picoline, 533
durene, 63	piperonal, 220
gallic acid, 230	chloride, 220
hydrindene, 387	pyridine, 533
hydroatropic acid, 255	quinazoline, 590
cinnamic acid, 256	quinoline, 547
indigo, 475	quinone, 163
indone, 385, 386	dicarboxylic ester, 305
iodacetophenone, 249	quinoxaline, 596
isodurene, 63	salicyl chloride, 224
menthane, 318	stilbene 270 275
nitro-acetophenones, 249	stilbene, 370, 375
	styrolene, 267
prehnitol, 63	tetraoxybenzene, 166
quinone, 163	thiophene, 454
chlorimide, 172	tolane, 37I
phenolimide, 173	Dichroines, 141
shikimic acid, 301	Dicumarketone, 383
stilbenes, 375	Dicyanaminobenzoyl, 212
styrolene, 267	benzene, 242
thiophene, 454	compounds, 439
Dicamphor, 328	diamide, 129
Dicarbobenzobis-phenylpyrazolon, 493	naphthalene, 409
phenylglyoxylic acid, 266	Dicyanogen compounds, 440
Dicarboxethyldiphenylcarbazide, 128	phenyl hydrazine, 130
Dichloracetophenone, 249	stilbene, 377
amidophenol, 153	Diesoanhydride of dioxyhydrobenzoin, 3
aniline, 92	Diethenyl azoxime, 515
benzenes, 59	Diethoxydiphenylmethane, 346
cinnamic acid, 275	quinoxime, 165
diazophenol, 153, 516	Diethylacetophenone, 189
amorphicity 133, 3-4	

Diethylamidophenol, 154	Diliydrocumic acid, 301
diphenyl tetrazone, 131	cymene, 294
Diethylene-diimide, 439	diethyl benzene, 294
diphenylamine, 79	
	diphenyl, 335
disulphide, 442	quinoxaline, 596
oxide, 442	tetrazine, 607
hexa hydrobenzene, 292	diphthalyldiimide, 376
indigo, 472, 475	eucarvone, 316, 319
ketohexamethylene, 296	eucarvylamine, 317
methylamido-pyrimidine, 588	fencholene, 324, 334
pyrimidine, 588	furfurane, 452
phenols, 145	glyoxalines, 498
phenosafranine, 603	indones, 385
	isocoumarin-carboxylic acid, 26
phthalide, 235	
protocatechuic acid, 228	392
succino-succinic ester, 305	phorol, 298
terephthalyl, 233	quinolines, 557
Diformazyl, 130	isoxylene, 307
Difurfural triacetophenone, 449	ketoindol, 469
Difuryl triazole, 512	ketoIndols, 470
Digallic acid, 231	methyl indol, 191
Digitaligenin, 431	isopropyl benzene, 294
Digitalin, 431	phthalazine, 586
Digitalinum verum, 431	naphthalene, 411
Digitalis lulea, 431	derivatives, 411
purpurea, 431	dibromide, 412
Digitalose, 431	naphthinoline, 558
Digitogenin, 431	naphthoic acids, 411
Digitonin, 43I	naphthol, 264, 392, 411
Diglycolanil, 84	oxazoles, 503
anilic acid, 84	phenanthridine, 558
Diglycollamid anhydride, 581	phenazine, 598
Diglycollo-imide, 581	
	phenazone, 587
Diglycolphenylamidic acid, 84	phentriazine, 115
Dihalogen anthracenes, 423	phthalic acid, 303
Dihaloid ethyl benzene, 266	pyrazine, 374
Diheteroatomic four-membered rings, 446	pyrazines, 593
three-membered rings, 444	p yrazole, 480
Dihippenylurea, 201	quinazoline, 181
Dihydrazino-biphenyl-disulphonic a c i d,	azolines, 590
339	quinoline, 545, 550
Dihydric aromatic alcohols, 232	quinoxalines, 373
phenols, 158	resorcin, 161
Dihydro-acetophorone, 296	resorcinol, 296, 307
acridin, 560	dioxime, 296
arecaïdine, 565	homologues, 297
benzaldehyde, 301	safrol, 270
benzene, 294	shikimic acid, 301
tetrabromide, 294	sparteine, 567
benzenes, 293	terephthalic acid, 304
benzoic, acid, 301	terephthalic acid cis-dimethyl est
camphene, 322	304
campholene lactone, 329	terephthalic acid dimethyl este
carboxylic acid, 170	304
carveol, 316	terephthalic acid transdiphenyl
carvone, 319	ter, 304
carvylamine, 317	toluene, 294
collidine dicarboxylic ester, 528	Dihydroxamic acid ethyl ether, 207
coumarone, 464	methyl ether, 207

Dihydroxylbenzyl pyridine, 289	Dimethoxytolane, 371
Dihydroxylene, 294, 432	Dimethylacridone, 560
Diimidonaphthol, 407	americ acid, 383
urazole, 514	amido-azo-benzene sulphonic acid
Diindogen, 469	138
Di-indoxyl, 476	benzaldehyde, 187
Diiodeinnamic acid, 275	hydrol, 344
cyclohexane, 295	ophenone, 347
diphenyl, 336	methyl coumarin, 282
Di-iodothymol, 144	nitrobenzhydrol, 344
phenol sulphonic acid, 156	phenol, 153, 154
styrolene, 267	phenyl glyoxylic ester,
Di-isonitroso-anethol peroxide, 250, 269	259
superoxides, 269	trichlorethyl al-
propyl-succino-succinic ester, 305	cohol, 252
Diketodiphenyl pyrrolidine carboxylic es-	pyrimidine, 588
ter, 462	triphenyl methane, 352
hexahydrobenzene carboxylic ester,	aniline, 78
307	ethyl iodide, 78
hexamethylene, 161, 168, 296	anisidine, 153
tetracarboxylic es-	anthracene, 423
	hydride, 424
ter, 307 hydrindene, 388	
	anthracenes, 423
carboxylic ester, 388 hydroindol, 471	anthrarufin, 428
	apionol, 166
julolidine, 552	aziethane, 439, 440, 446
methyl lilolidine, 552	benzamide, 199
pentachlorhexene, 162	chloride, 203
Diketone carboxylic acids, 261	benzoic acid, 195
Diketones, 233	benzyl alcohol, 177
penthiazolidine, 583	biphenyl-dicarboxylic acid, 341
piperazines, 594	caffeic acid, 283
pyrazolidine, 480, 481, 491	carbazole, 477
pyrrolidine, 480	coumalic acid, 522
pyrrolidines, 462	coumalin, 522
tetrahydroglyoxalines, 499	coumarin, 282
naphthalene derivatives,	coumarone, 464
413	cyclohexandion, 297
naphthylene oxide, 405,	hexane, 292
413, 444	diamidotoluphenazine, 599
pyridazine, 586	dihydroIndol, 470
quinazolines, 592	resorcinol, 297
quinoline, 213, 470	dihydroxy-heptamethylene, 29
thiazole, 507	diketohexamethylene, 297
acetic acid, 507	hydrindene, 388
triazolidine, 514	diphenyl tetrazone, 131
Dill oil, 320	furazane, 515
Dimesitylmethane, 343	furfurane, 447, 448
Dimethoxyanthranilcarboxylic acid, 238,	carboxylic acid, 451
242	dicarboxylic acid, 451
benzoic acid, 228	gentisin alcohol, 218
diphenyl methane, 346	hydrothymoquinone, 163
phthalaldehydic acid, 237	indazole, 493
azone, 237	indol, 466
phthalic acid, 242	carboxylic acid, 468
anhydride, 241	indolinon, 471
phthalide, 235	isindazole, 493
pyridine, 534, 588	isophthalate, 242
quinone, 170	isoxexolon, 495

methylketohexamethylene, 296	Dinitranilines, 93
hexene, 298	Dinitratifiles, 93 Dinitroanthracene, 423
methyl imido-thiazole, 505	quinone, 425
naphthalene, 394	azobenzene, 113
naphthol, 400	azoxybenzene, 112
naphthophenoxazime chloride,	benzene-azobenzene, 113
582	benzenes, 66
nicotinic acid, 536	benzidine, 337
oximide chloride, 497	henzophenone, 347
oxypyrimidine, 588	benzyl acetic acid, 379
phenolphthalein, 364	benzidine, 337
phenosafranine, 603	brom pyrrol, 459
phenylene diamine, 116	chlorbenzene, 67
green, 174	cinnamic acid, 278
phenylimido-oxalic ester, 91	diacetdiamido-diphenyl, 337
urazole, 514	dibenzyl, 370
piperazine, 594	diethyl hydroquinone, 164
protocatechuic aldehyde, 220,	dioxyquinoline, 575
270	diphenic acid, 341
pyrazine, 593 pyrazole, 482	diphenyl, 336
carboxylic acid, 485	amine, 93 diphenylene oxide, 476
pyridine, 532	methane, 343
dicarboxylic acid, 537	phthalides, 363
pyridone, 534	durenes, 68
carboxylic acid, 538	hydrocinnamic acid, 211
pyrone, 522	mellitic tetraethyl esters, 246
dicarboxylic acid, 523	quinone, 164
pyrrol, 447	diacetate, 164
carboxylic acid, 461	naphthalenes, 396
dicarboxylic acid, 461	naphthol, 401
quinite, 295	oxanilide, 91
quinoline, 191, 543, 546, 589	oxyphthalic acids, 241
quinoxalone, 596	pyridines, 533
selenophene, 456	phenol, 150
terephthalic acid, 243	ether, 146
tetrahydrobenzene, 293 pyrone dicarboxylic di-	phenols, 150 phenyl acetoacetic ester, 260
ethyl esters, 523	diazosulphide, 103
thiazole, 505	malonic ester, 262
thiophene, 447, 454	nitrosohydroxylamine, 70
tolane, 37I	pyridine, 532
tolimidazole, 501	phthalic acid, 243
toluquinoxaline, 596	pyrrol, 459
umbelliserone, 283	resorcin, 161
naphthacridone, 560	Dinitrosobenzenes, 70
naphthol methane, 410	naphthalenes, 396
naphthoxanthene, 410	resorcinol, 161
anthones, 525	toluene, 70
naphthylamine, 396	Dinitrostilbenes, 370
carbazole, 478	styrolene, 268
carboxylic acid, 417 derivatives, 409	thiophene, 454 tolyl methyl nitramine, 99
naphthylene-methanes, 417	xylene, 68
thiophene, 476	Diolefine benzenes, 268
ethers, 400	Dioxethyl benzene 233
methane derivatives, 409, 410	Dioxindole, 251, 471
sulphides, 404	Dioxosuccinic ester, 122
nicotinic acid, 537	Dioxyalcohol acid, 255

-3-	
Dioxyamidocyanidine, 605	Dioxypyridines, 534
anthracenes, 423	quinoline, 549
anthranol, 424	quinone, 170
quinone, 427	dicarboxylic ester, 306
	dihydro-carboxylic ester,
quinoline, 554	
quinones, 426	306
benzaldehydes, 219	quinoxaline, 596
aldiketohydrindene, 388	quinoyl, 171
benzene, 159	stilbene, 371
benzoic acids, 227	tartaric acid, 159
phenone, 168, 348	terephthalic acid, 243
benzyl alcohols, 218	ethyl ester, 243
amine, 218	terpineol, 316
biphenyl, 339	tetranitroanthraquinone, 432
cinnamic acid, 282, 283	zotic acid, 519
coumarin, 283	acids, 205
dihydroshikimic acid, 301	thymoquinone, 170
diketotetrahydronaphthalene, 393	toluene, 161
dimethyl triphenyl methane, 360	toluic acids, 229
diphenyl methane, 343	triphenyl-carbinol, 360
phthalide, 364	methane, 359
sulphone, 139	carboxylic acid,
tetrazolium betaine, 521	362
diquinoylbenzene, 171	methanes, 359
durylic acid, 229	xanthone, 525
hexahydroisophthalic acid, 304	xylene, 161
isophthalo-nitrile, 297	Dipentene dihydrobromide, 312
terephthalic acid, 304	chloride, 311
hydrindene, 387	iodide, 312
hydrocampholenic acid, 328	group, 310
fluorane carboxylic acid, 362	nitrosochloride, 312
isonicotinic acid, 538	tetrabromide, 312
mesitylene, 162	Diphenacyl, 380
methyl cinnamic acid, 283	acetic acid, 383
methylanthraquinone, 428	acetoacetic ester, 383
monocarboxylic acids, 227	malonic ester, 383
naphthalene, 404	Diphenamino-acid, 341
naphthalenes, 403	Diphenhomazine, 436
quinone, 404, 405	Diphenic acid, 337, 340
naphthoic acid, 409	anhydride, 341, 4 36
quinone, 396, 405	chloride, 341
quinoxaline, 596	Diphenimide, 341, 415, 436
naphthyl sulphide, 404	Diphenine, 117
phenanthrene, 415	Diphenoldisulphide, 160
phenazines, 600	ethane, 368
phenylaceticdicarboxylic triethyl	Diphenols, 143
ester, 306	Diphenoxyacetic acid, 146
aceto-dicarboxylic ester, 246,	Diphenyl, 335
307	acetaldehyde, 368
acrylic acid, 282	acetic acid, 229, 368
anthranol, 424	acetoacetic acid, 380
fatty acids, 229	nitrile, 368
olefine carboxylic acids, 282	acetylene, 371
propionic acid, 229, 230	allophanic acid, 86
phthalaldehydic acid, 237	amidine-thiomethyl, 87
phthalic acid anhydride, 241	amidocyanidine, 605
picoline, 535	amidoxazoline, 503
picolinic acid, 538	amine, 71, 79
pyridine carboxylic acid, 538	blae, 359
• • • •	

phenyl aminol methane, 344	1
anthrone, 424	1
azophenylene, 80, 173	
benzamide, 200	ł
benzene, 341	
benzylsultam, 353	١
biuret, 86	1
brommethane, 344	-
	-1
butane, 380	- 1
group, 380	-
butylene, 380	1
butyrolactone, 380	-1
carbazide, 127	-
carbinol, 344	ı
chloride, 344	-
chlormethane, 344	-
triazole, 512	١
cresol, 359	-
crotolactone, 377	-
cyanamide, 90	- 1
diacetylene, 380	
diacipiperazine, 84, 594	1
dichlor-ethane, 368	- [
methane, 345	١
ethylene, 380	
hydrazimethylene, 445	- [
hydro-diphenyl pyrazine, 593	
tetraazine, 205, 206	ı
isoIndol, 593	
ketohexane, 383	
nonane, 383	- 1
octane, 383	
piperazine, 594	- !
methyl ethane, 370	
pyrazine, 593	
tetrahydropyrone, 523	
nitro methane, 346	
selenide, 158	
iphenylene acetic acid, 419	
diamine, 338	
hydrazine, 337	
ketone, 425	
phenyl ethane, 418	
ethylene, 418	
pinacoline, 418	
succinic anhydride, 418	
selenide, 160	
sulphide, 157	
sulphone, 160	
glycollic acid, 415, 419	i
imide, 462, 477	
ketone, 415, 419	
carboxylic acids,	
419	١.
dicarboxylic a c i d,	
416, 420	. !
oxides, 524	-
methane, 417	
oxide, 143, 462, 463, 476	

```
Diphenylene phenylmethane, 418
             sulphide, 158, 336, 462, 463,
                476
             sulphone, 476
Diphenyl ethane, 367
                 derivatives, 367
                 group, 369
          ethenyl-amidine, 83
          ethylene, 368, 370
                    diamine, 372
                    glycolmononitrite, 368
          fluorindene, 604
          formamidine, 82,83
          furazane, 374, 515
          furfurane, 380, 449
                     dicarboxylic ester,
                       382
          glycollic acid, 369
          glyoxal, 373
          glyoxaline, 498
                      mercaptan, 498
          glyoxylic acid hydrazone, 258
          guanidine, 88
hexane group, 383
          hydantoin, 86
          hydrazine, 116
          indol, 373
indone, 386
Diphenyline, 338
Diphenyl iodonium hydroxide, 60
                    iodide, 60
          isodihydrotetrazine, 126, 607
          isoxazole, 494
          itaconic acid, 369
           ketipic acid, 382
           ketocyclopentene acetic acid, 28
          dihydro-triazine, 126
          ketone, 345
           ketotetrahydrotriazine, 605
          lævulinic acid, 382
          maleic acid, 252, 377
           methane, 369
                     carboxylic acid, 349
                     dicarboxylic acid, 349
           methanes, 342
methyl-benzaldehyde, 361
                   cyanidine, 205, 604
                  ethyl glyoxaline, 496
                   oxazole, 502, 503
                  pyrazole, 481
                   pyrazoline, 273
           monochlor-ethane, 368
                      ethylene, 368
           nitrosamine, 98
           octan-dion, 377
oxalyl diacetic acid, 382
           oxazole, 251, 503
           oxide, 146, 336
```

oxybiazole, 374, 516

03-	
Diphenyl oxycrotonic acid, 380	Diphenyl vinyl-benzoic acid, 378
cyanidine, 205, 605	dinitrite, 368
ethylamine, 372	ethyl ether, 368
triazine, 605	nitrite, 368
	xylylmethanes, 351
parabanic acid, 91	Diphthalic acid, 341
pentane group, 383	Diphthalide ether, 237
phenylene, 341	Diphthalul ethena 288
phosphine chloride, 132	Diphthalyl ethene, 388 Diphthyl, 376
phosphinic acid, 132	
phthalides, 362, 363	Dipicolinic acid, 537
piperazine, 79, 594	Dipiperidyl isatin, 472
piperidine, 540	Di-propyl succino-succinic ester, 305
propane, 378	Diprotocatechuic acid, 227
propionic acid, 369, 376	Dipterix odorata, 281
pyrazine, 593	Dipyridyl, 533
pyrazole, 273, 483	Dipyrryl ketone, 460
carboxylic acid, 485	Diquinolines, 547
ester, 484	Diquinolyl-quinoline, 547
pyrazolon, 260	Diquinoyldioxime, 161
pyridine, 532	tetraoxime, 172
pyrrol, 380	Diresorcinol, 161
carboxylic acid, 461	Disazoamido-compounds, 64
dicarboxylic ester, 461	compounds, 112
quinoxaline, 596	Disdiazoamido compounds, 106
selenide, 140, 158	benzene amide, 107, 109
selenium oxide, 139	anilide, 109
selenone, 140	methylamine, 109
succinic acid, 377	Disulphanilic acid, 137
sulphide, 140	Disulphobenzoic acid, 216
sulphocarbazide, 128	cyanides, 97
carbazone, 114, 128	Disulphoxides, 138
carbodiazone, 128	Ditertiary-amyl-hydroquinone, 163
sulphone, 140	resorcinol, 161
sulphoxid e, 139, 140	Dithiënyl, 454
tellurid e, 158	ketone, 455
tetrahydrophenyl pyrazine, 594	methane, 454
p y r o n e-dicarboxylic-	phenyl methane, 454
diethyl esters, 523	Dithiobenzoic acid, 199
quinoxaline, 597	hydroquinone, 164
ketone, 381	urazole, 514
ketoxime, 381	Ditoluene sulph-hydroxamic acid, 135
zine, 206, 607	Ditolyl, 336
zole, 206, 520	amines, 79
zolium chloride, 520	imide, 477
carboxylic	isodihydrotetrazine, 607
acid, 520	ketone, 345
hydroxid e, 131, 520	oxybiazole, 516
thiocarbonic ester, 148	phthalides, 363
phene, 380, 454	urea chloride, 85
thiurea, 85, 87	Diurea, 607
tolyl carbinol, 353	DiureInes, 374
methane, 351	Divinyl benzene, 268
triazole, 512	Dragon's blood, 193
azolon, 513	Dryobalanops camphora, 324
chlor-ethane, 368	Durene, 55
ketone, 379	Duroquinone, 169
urazine, 127, 128, 607	Durylic acid, 196
urea, 85, 207	quinone, 229
chloride, 85	Dypnone, 189, 379
· · · · · · · · · · · · · · · · · · ·	

E.	Ethyl benzoylacetic ester, 260
Ecgonine, 541, 570	benzyldioxy pyridine, 535
Eikonogen, 403	carbazole, 477
Ellagic acid, 230	chavicol, 269
Emodin, 428	cinnamic acid, 278
Emulsin, 430	coumarin, 282
Eosin, 366	cyclopentene carboxylic acid, 570
scarlet, 366	diphenyl, 336
Epichlorhydrin, 481	Ethylene benzamidine, 499
Erythrin, 229	dibenzamide, 200, 204
Erythrol, 229	phenyl diamine, 79
tetrabenzoate, 198	disulphone, 139
Erythro-oxyanthraquinone, 426	thioethidene, 478
Erythrosine, 366	ethidene ether, 478
Esters of glycol, 441	imide, 438, 440, 444
of monobasic aromatic acids, 197	isobutylidene-diphenyl- diamine,
of trimethylene glycol, 442	
	79
Estragol, 268, 269 Estragonal oil, 269	naphthylene, 410
	oxide, 437, 440, 444
Ethane-dibenzoyl-dicarboxylic acid, 382	phenylhydrazine, 121
Ethenyl amidophenol, 153, 504	urea, 85
amido-thiophenol, 83, 157	protocatechuic acid, 228
benzenyl azoxime, 208, 515	selenurea, 508
phenylhydrazidine, 129	succinic acid, 129
Ethers of the nitroso-naphthols, 406	sulphide, 438, 440, 444
Ethidene aniline, 79	thiourea, 499
diacetoacetic ester, 62	urea, 499, 503
dibenzamide, 200	Ethyl gallic ester, 230
ethylene disulphide, 441	glyoxalidine, 499
phthalide, 286	glyoxaline, 498
thiourea, 446	indene, 385
urea, 439, 446	indol, 467
Ethine diphthalyl, 382	indoxyl, 469
Ethoxy acetamidoquinoline, 547	indoxylic acid, 469
benzidine, 340	ester, 469
benzothiazole, 86, 508	isatin, 467, 472
benzoxazole, 504	isindazole acetic acid, 277, 493
cinnamic ester, 287	isocarbostyril, 556
cyanaminobenzoyl, 212	diphenyl urea, 86
lutidine, 534	quinoline, 556
methylene aniline, 82	thioacetanilide, 83
methyl indol, 470	mercapto triazole, 512
mustard oil, 86, 508	mesitylene, 56
phenyl carboxylic ester, 588	naphthalene, 394
pyridazone, 585	orthobenzoate, 208
succinamide, 154	phenanthridine, 558
pyridine, 534	phenazonium iodide, 600
tolimidazole, 502	phenols, 144
Ethyl acetanilide, 82	phenyldithiomethane, 86
amido cinnamic acid, 277	ether, 146
triazsulpholes, 518	hydrazine, 121
aniline, 78	methylpyrazolon, 488
anthracene, 423	propiolic ester, 284
benzene, 54	amide, 284
benzoic acid, 195	chloride, 284
ester, 198	urea, 85
benzoin, 372	piperic acid, 285
quinone, 169	piperyl alkine, 535, 564
benzoxazolon, 504	pyridine alkine, 564
, , , ,	Education of the A

Furfuraldoxime, 449
lævulinic acid, 463
monoacetophenone, 449
Furfuramide, 450
amidine, 205
Furfurane, 437, 441, 447, 448, 462, 479
carboxylic acid, 450
 dicarboxylic acid, 451
group, 447
angelic acid, 450
Furfurin, 450, 499
Furfur-malonic acid, 450
Furfurodiazoles, 515
Furfurol, 73, 443, 449
lævulinic acid, 450
Furfuro-stilbene, 449
Furfur-propionic acid, 450
valeric acid, 450
Furfuryl alcohol, 449
amine, 449
methyl ether, 449
nitrile, 451
Furil, 449
Furilic acid, 449
Furo-diazole, 479, 514
diazoles, 480, 514, 516
Furoin, 449
Furol, 449
Furomonazole, 493
group, 493
monazoles, 479, 502
Furon-aldehyde, 450
Furyl tetrazole, 520
G.
Galbanum, 160, 283
Gall-acetophenone, 221
Gallein, 366
Gallic acid, 230

Gallipot resin, 334 Gallobromol, 230 carboxylic acid, 244 chlor-acetophenone, 249 cyanine, 582 Gallyl-gallic acid, 231 Garancin, 427 Gelsemium sempervirens, 431 Gentiseln, 525 Gentisin, 433, 525 aldehyde, 220 Gentisinic acid, 229 Geranic acid, 310 Geraniol, 310 Geranium oil, 309 Glucomethyl-cumar ketone, 273 Glucose, 429, 430

pentabenzoate, 198

Glucosides, 429 Glutaconimide, 534 Glutaric anhydride, 437, 442 Glutarimide, 438, 442 Glutazine, 535 Glycerol tribenzoate, 198 Glycide derivatives, 444 Glycocoll, 137 Glyco-cumar alcohol, 271 cumaric aldehyde, 272, 430 Glycol-chlorhydrin, 411 dibenzoate, 198 diphenyl ether, 146 Glycolide, 444 monophenyl ether, 146 phenyl urea, 86 Glycosine, 497 Glycosides, 429 vanillin, 430 Glyoxal bisulphite, 468 ethylin, 497, 498 Glyoxalidines, 498 Glyoxaline dicarboxylic acid, 498 group, 439, 441 Glyoxalines, 96, 373, 479, 496 osotetrazone, 124 propylin, 497, 498 Glyoxime hyperoxide, 442 Green oils, 49 Grénat soluble, 151 Guaiacol, 159 Guanazole, 514 Guanazyl benzene, 206 Gum benzoin, 193 lac, 334 resins, 334

H.

Guvacine, 565

HÆMATEIN-AMMONIA, 433 Hæmatin, 433 Hæmatoxylin, 433 Hamatoxylon campechianum, 433 Hair, 253 Haloid acetophenones, 190 anhydrides of aromatic acids, 198 benzaldehydes, 186 nitrophenols, 151 pyrazoles, 483 Heavy oil, 49 Hedeoma pulegoides, 320 Helianthine, 95, 138 Helicin, 272, 430 Heliotrope, 98 Heliotropine, 220, 270 Hemellitic acid, 195

Hemimellibenzyl alcohol, 177

Hemimellibenzylamine, 179	He
mellithene, 55	
mellitic acid, 245	
pinic acid, 241	
anhydride, 241	
ternene, 307	
terpene, 307 Heptacarbocyclic compounds, 28	
chlor-cyclohexandion, 297	
ketotetrahydrobenzene, 298	
resorcinol, 161, 297	
methylene, 28	
terpene, 28	
naphthene, 292	
Hesperetol, 269	
Hesperidin, 283, 311, 430, 432	
Hesperitinic acid, 283	
Hetero-atoms, 435	
cyclic carbon derivatives, 95	Î
compounds, 435	
derivatives, 17	
ring formations, 122, 126, 127, 128,	
129, 130, 131	
of amidoximes, 208	
of anthranilic acid.	
ara	
Hexabromtriketo-hexylene, 297	
carboxylic compounds, 20	
Hexacetyl derivatives, 166	
chlor-a-oxycyclopentene carboxylic	
acid, 27	
benzene, 59	
cyclohexandion, 297	l
diketoherene 150 160 eee	l
diketohexene, 159, 169, 299 ketodihydrobenzene, 299	1
	l
R-pentene, 26, 45 oxypentene carboxylic acid, 387	i
pentane aument a milione id	l
pentene oxycarboxylic acid, 45	1
triketo-hexylene, 165, 297	ł
ethyl benzene, 57	l
hydric phenols, 166	1
hydroanthranilic acid, 300	1
benzene, 290, 291, 307	1
hexacarboxylic acids,	1
307	l
benzodipyrazolon, 493	1
benzoic acid, 300	1
amide, 300	i
ethyl ester, 300	l
methyl ester, 300	1
carbazole, 478	
cinchomeronic acid, 540	He
cumene, 292	Hi
cymene, 292, 313	Hi
dicarboxylic acids, 302	Hi
diethyl phenol, 294	Hi
dimethylnaphthalene, 433	Hi
Dhenol, 204	Ι΄
dioxybenzoic acid, 301	1
hexaoxybenzene, 295	1 Hi

```
xahydroisophthalic acid, 302
mellitic acid, 307
        naphthalene, 413
naphthinoline, 558
oxybenzoic acid, 301
            toluic acid, 315
        phenol, 294
phthalic acids, 302
anhydride, 302
        pseudocumene, 292
        pyrazines, 594
pyridine, 538
        quinoline, 545, 551
quinolinic acid, 540
        salicylic acid, 301
        terephthalic acids, 303
        tetraoxybenzoic acid, 301
        toluene, 53, 298
toluic acid, 300
        trioxybensoic acid, 301
        xylene, 292
 iodbenzene, 60
 keto-hexamethylene, 171, 297
  methoxy-aurine, 361
  methoxybenzil, 369, 375
            benzilic acid, 375
  methoxyl-rosaniline, 361
  methyl benzene, 56, 57
  methylene, 292
  methylene carboxylic acid, 300
               dicarboxylic ester,
                  307
              tetracarboxylic acid, 3
              tetracarboxylic ester,
  methyl-leucaniline, 78
          pararosaniline, 357
          phloroglucin, 165
           triamidotriphenyl carbin
                                 358
                                metha
                                 358
             ketohexamethylene, 16
  nitrodiphenylamine, 93
  oxybenzene, 166
      biphenyls, 339
      diphenyl, 340
  phenylmelamine, 90
          pararosaniline, 359
          rosaniline, 80
xyl phenyl ketone, 189
pparaffin, 200
openyl urethane, 201
ppuramide, 555
ppurazide, 200, 201
ppuric acid, 200
       anhydride, 200
       phenyl ester, 200
ppuroflavin, 200
```

puryl-hydrazine, 200	Hydrazioxalyl, 436
phenylbuzylene, 131, 202	propionic methyl ester, 445
fmann's violet, 358	pyrazolon, 489
matropine, 567	carboxylic acid, 489
moantipyrine, 488	Hydrazobenzene, 116, 117
benzoylated paraffins, 190	disulphonic acid, 138
caffeic acid, 283	benzoic acid, 215
camphoric acid, 333	bodies, 112
ferulic acid, 283	compounds, 116
isophthalic acid, 244	zoic acid, 110, 201
linalool, 310	naphthalene, 398
mologous anthraquinones, 425	toluenes, 117
cinnamic acids, 278	ximes, 124
dioxyanthraquinones, 428	xylenes, 117
furfurane carboxylic acids, 451	zulmin, 446
indols, 466	Hydrindene, 384, 387
naphthalene carboxylic acids,	carboxylic acid, 265, 387
408	derivatives, 385, 387
phenyl glyoxylic acids, 259	dicarboxylic acid, 387
phenyl gryoxyne acids, 259 phenylhydrazines, 120	ethyl ketone, 387
pyrazoles, 481	glycol, 387
rosanilines, 357	methyl ketone, 387
series, 437	phenyl ketone, 387
trioxyanthraquinones, 428	Hydrindone, 387, 388
mologues, 31	azine, 387
mooxybenzaldehyde, 219	Hydrinic acid, 251
phthalic acid, 238, 244	Hydroanthracenes, 424
phthalimide, 244	anthranol, 425
phthalonitrile, 244	antipyrine, 49
piperonylic acid, 229, 270	aromatic carboxylic acids, 299
protocatechuic, 229	derivatives, 18
pyrocatechol, 160	hydrocarbons, 290
salicylic aldehyde, 219	ketone carboxylic acid, 47
saligenin, 217	keto chlorides, 159
terephthalic acid, 244	nucleus, 410
terpenoylformic acid, 324	substances, 29
terpenylic acid, 324	terpenes, 308
methyl ketone, 324	atropic acid, 278
vanillic acid, 229	benzamide, 184, 497
vanillin, 270	benzene derivatives, 290
orn, 253	tetracarboxylic acids, 306
rdrastic acid, 242	tricarboxylic acids, 306
tine, 578	benzoIn, 371, 372
tinine, 578 -	caffeIc acid, 229
tropic acid, 197	dimethyl ether acid, 230
nitrile, 203	methylene ether acid, 230
ydraziacetic acid, 445	camphorylacetic acid, 333
benzil, 373	malonic acid, 333
zide, 363	carbazoles, 477
dines, 129, 205	carbons, 351
methylene, 445	carbostyril, 214, 551
zine anisol, 155	carboxylic acid, 551
benzoic acids, 215	chelidonic acid, 522
cinnamic acid, 277, 492	chloranilic acid, 166
compounds, 116	cinchonic acid, 537
derivatives of naphthalene, 398	cinnamenyl acrylic acid, 278
phenols, 155	cinnamic acid, 191, 197, 284
zines, 63	carboxylic acid, 245, 265,
zino-diphenyl, 339	393
	973

Hydrocinnamic nitrile, 203	Hydroumbellic acid, 230
cinnamide, 272	xyloquinone, 163
anti-oxime, 272	Hygric acid, 462, 570
phenyl hydrazone, 272	llygrin, 462, 570
syn-oxime, 272	Hyoscyamine, 253
cinnamyl alcohol, 177	Hypnone, 189
coerulignone, 339	Hystazarin, 159, 428
cornicularic acid, 262, 382	
cotoln, 349	
coumaric acids, 226	I.
coumarilic acid, 253, 280, 464	Idryl, 420
coumarin, 227	Illicium anisatum, 269
coumarone, 217	religiosum, 270, 301
coumoquinone, 163	Imesatins, 472
cyanic acid, 430	Imidazole dicarboxylic acid, 497
pararosaniline, 369	Imidazoles, 96, 479, 480, 496, 497, 502
rosaniline, 369	Imidazolon, 499
ecgonidine, 571	Imidazolyl mercaptan, 498
euthiochronic alkali salts, 166	methyl sulphide, 498
ferulic acid, 230	Imido-benzimidazolines, 502
furfuranes, 451	benzophenone, 346
glyoxalines, 498	benzoyl cyan-methane, 260
hydrastinine, 578	coumazones, 581
Indol derivatives, 470	coumothiazone, 583
isindazole derivatives, 493	Imidodiketotetrahydroglyoxalines, 499
isocarbostyril, 557	glutarimide, 535
ferulic acid, 230	ketone naphthalenes, 407
quinolines, 557	ketotetrahydrothiazole acetic aci
	•
juglones, 404	507
lytic condensations, 43	oxybiazolines, 516
methyl ketol, 470	naphthalenes, 407
naphthalene derivatives, 410	naphthalene-sulphonic acid, 4
naphthoquinone, 403	phenylcarbamic thiomethyl ester,
nitric acid, 110, 111	oxide, 153
paracoumaric acid, 254	uracil, 260
phorone, 163	tetrahydro-oxazoles, 503
piperic acid, 283, 285	selenazole, 508
pyridine derivatives, 538	thiobiazolines, 517
pyrimidines, 588	urazole, 514
pyrrols, 461	Inactive mandelic acid, 251
quinolines, 550	pinene, 322
quinone, 159, 162	quinic acid, 301
bisoxychlorphosphine, 163	tropic acid, 253
carboxylic acid, 229	
chlorphosphine, 163	Indamines, 174
	Indazine, 603
diacetate, 163	Indazole acetic acid, 493
diethyl ether, 163	carboxylic acid, 493
methyl ether, 163	Indazoles, 277, 480, 491, 492, 509
ethyl ether, 163	Indazolon, 493
quinones, 167, 366	Indene, 384
quinone, substitution products of,	carboxylic acid, 386
163	nitrosites, 385
tetracarboxylic ester, 246	Indenigo, 388
quinoxalines, 596	Indican, 473
quinoze dibenzoate, 163	Indigo, 74, 256, 258, 433, 443, 463, 40
resorcyclic esters, 305	470, 471, 473
terpenes, 308, 313	
	blue, 284, 465, 473
telrazones, 131	brown, 473
toluquinone, 163	carmine, 476

	INT
Indian disembandia said 486	
Indigo dicarboxylic acid, 476 fera anil, 74	
gluten, 473	
purpurin, 476	
red, 473, 476	
salt, 475	
sulphonic acid, 469	
Indigotin, 473	
disulphonic acid, 476	
monosulphonic acid, 476	
Indigo white, 476	
Indin, 476	
Indirubin, 469, 476	
Indoanilines, 173	
amine, 96	
Indogen, 469 Indogenides, 469	
Indogen oxide, 469	
Indol, 74, 124, 268, 370, 462, 463, 465	
carboxylic acids, 468	
condensation, 127	
derivatives, 487	
Indolinons, 470	
Indone, 385, 600	
Indophenazine, 472	
phenin, 472	
reaction, 452	
phenol, 96, 173, 407	
Indoxanthic ester, 469	
azene group, 495 azenes, 480	
Indoxin, 470	
Indoxyl, 468, 469	
Indoxylic acid, 468, 469	
ester, 284	
Induline dyes, 173	
Indulines, 115, 580, 600	
Inosite, 295	
hexaacetate, 295	
Iodacetophenone, 190	
Iodbenzaldehyde, 186	
Iodbenzenes, 59 Iodbenzoic acid, 209	
Iodeinnamic acid, 276	
Iodcyclohexanol, 295	
Iodhydrocinnamic acid, 254	
Iodine greens, 358	
Iodisophthalic acid, 242	
Iodmandelic acid, 251	
Iodnaphthalenes, 395	
Iod-naphthalic acid, 405	
Iodnitrohydrindone, 387	
Iodobenzene, 60	
Iodol, 459	
of tetramethyl rosanili	
	iiC
iodide, 358 Iodosobenzaldehyde, 186	
benzene, 60	
,	

Iodosobenzene sulphonic acid, 137 benzoic acids, 209 naphthalenes, 395 Iod-oxynaphthoquinone, 405 Iodphenol, 149 Iodphthalic acids, 241 Iod-pyrazole, 483 Iod-quinoline iodmethylate, 547 Iodsalicylic acid, 225 Iodthiophene, 454 Iodtoluene, 62 Ionone, 310 Iregenone dicarboxylic acid, 266 tricarboxylic acid, 266 Iretol, 166, 431 Iridic acid, 164, 231 Iridin, 431 Iridol, 164, 431 Iris florentia, 431 Isamino-camphor, 329 Isantipyrine, 489 Isapiol, 166, 271 Isatid, 471 Isatin, 258, 284, 470, 471 Isatinates, 258 blue, 472 carboxylic acid, 392 chloride, 472 semicarbazone, 472 Isatinic acid, 258 lactam of, 258 Isatogenic acid, 284, 445 ester, 260, 469 Isatoic acid, 212, 471 Isatoxime, 472 Isatropic acid, 278 Isindazoles, 492 Isoacetophorone, 298, 307 allyl benzene, 268 amyl phenyl ketone, 189 pyrrol, 458 anthraflavic acid, 428 benzalphthalide, 376 phthalimidine, 557 benzil, 375 benzofurfurane, 463 pyrrol, 463 thiazol, 441 thiophene, 463 benzyldiphenyl, 350 bidesyl, 381 borneol, 325 acetate, 321, 325 butyl anthracene, 423 chlorphthalazone, 586 desoxybenzoin, 371 butylidene methyl phenyl hydrazine, phthalide, 286

~ ~	
Isobatyl phenyl ketone, 189	Isonitroso campher, 329
phthalasone, 586	compounds, 487
salicylic aldehyde, 219	desoxybenzola, 371
butyrylacetophenone, 250	hydrindone, 387
methyl phenylhydrazide, 471	methyl-isoxazoloa, 495
campholic acid, 328	phenylacetic acid, 258
camphor, 330	propiophenose, 260
	ругаловов, 487
camphoric acid, 332	orcin, 162
camphoronic acid, 323, 329	oxalyklibensylketone, 381, 382
caprolactone, 324	oxycumic acid, 226
carbopyrotritartaric acid, 451	phendihydrotetrazines, 606
styril, 286, 556 carboxylic acid, 290, 556	phenyl naphthophenasonium chlorid
	600
carveol, 317	phorone, 298
carvone, 321	
chryso-fluorene, 418	phthalaidehyde, 233 dioxime, 233
cinchomeronic acid, 537	phthalic acid, 242
conicine, 565	
conine, 565	phthalophenone, 351
coumarin, 285, 285 , 523	phthalyl dichloride, 242
carboxylic acid, 290	dihydrazide, 242
cyanphenyl chloride, 83, 89	prene, 307, 309, 311
cyclic derivatives, 17	propylamidobenzyl alcohol, 470
dehydracetic acid, 522	benzene, 55
diazobenzene potassium, 98	benzoic acid, 195
bensenes, 69	coumarin, 288
hydrates, 103	dihydrobenzoic acid, 301
salts, IOI	isocarbostyril, 556
dihydrodiphenyl tetrazine, 607	mandelic acid, 252
phen-tetrazines, 115	phenol, 144
nitroresorcin, 161	pyridine, 532
phenic acid, 341	pyrrol, 459
phenylbenzene, 341	thiophene, 454
dihydrotetrazine, 206	propylidene, 495
oxyethylamine, 372	pulegol, 310
durene, 55	pulegon, 296
duridine, 76	purpuric scid, 151
durylic acid, 55, 196	purpurin, 428
eugenol, 270	quinoline, 272, 286
methyl ether, 259, 270	group, 244, 554
fencholen alcohol, 325	rosindone, 602
fenchonoxime, 334	rosindulines, 602
ferulic acid, 282, 283	safrol, 144, 270, 259
geranic acid, 301, 310	tetrahydropyromellitic acid, 306
hexahydromellitic acid, 307	thujonamine, 317
homopyrocatechol, 160	thujone, 319
hydrobenzoin, 371, 372	valerophenone carboxylic acid, 238
indol, 248, 463	vanillic acid, 228
ketocamphoric acid, 329	vanillin, 220
lauronolic acid, 332	Isoxazole, 479, 480, 493
Isologous series, 440	
menthorime as 8	carboxylic acids, 494
menthoxime, 318	ester, 494
Isomerisms of pentilene derivatives, 32	group, 439, 441
Isomerisms of naphthalene derivatives,	Isoxazolons, 259, 495
390	Isoxylene, 53, 54
naphthazarine, 405	Isoxylic acid, 195
nicotinic acid, 536	-
nitrososcetophenone, 189, 249, 257	J.
benzoyl acetone, 250	' Jalapin, 431

INDI	EX. 641
,	
Japan camphor, 308, 324, 327	Kino-tannin, 232
Jara-jara, 400	Knorr's pyrazoline reaction, 482, 486
Juglans regia, 404	Kynurenic acid, 550
Juglone, 405	Kynuric acid, 212
Juglonic acid, 241, 405	Kynurine, 549
Julin's chloride of carbon, 59	
Julole compounds, 552	
Julolidine, 552	L.
Juniper berry, 322	Lacmoid, 161
ļ	Lactam ethers, 504
	Lactams, 441, 442, 471
K.	of amidophenyl fatty acids, 214
Kairine, 551	Lactazam formation, 127
Kairoline, 551	Lactazams, 259
Ketine, 593	Lactazones, 495
Keto-benzimidazolines, 502	Lactic ethidene ester, 478
chlorides, 143	Lactime ethers, 504
coumaran, 464	of isatinic acid, 258
derivatives of the pyrazolidines, 490	Lactimides, 444
dihydro-acridine, 560	Lactone derivatives of fluorescein, 366
benzothiazine, 583	of phenolphthalein,
coumarone, 464	364
cymene, 320	I.actones, 441, 442, 446
Indol, 471	Lactoximes, 259, 495
naphthoic acid, 408	Lactyl tropeine, 568
pyrazoles, 486	Lævomandelic acid, 251
quinazolines, 213, 590 Ketoglyoxalidines, 499	tropic acid, 253
	Lævulinic acid, 236
hexahydro-cymene, 62, 318	phenylhydrazine, 127
methylene, 296, 307	Lakes, 426
carboxylic ester, 302,	Laurobenzene, 190
307	Lauronolic acid, 332
dicarboxylic acid, 304	Laurus camphora, 327
hexanes, 294	Lauth's dyestuffs, 96
hydrazones, 122	violet, 584
hydrobenzene dicarboxylic acid, 304	Lead tetraphenyl, 133
imido-tetrahydrothiazole, 507	Leaf green, 434
isocamphoric acid, 323	Lecanora, 162
menthans, 318	Lepidene, 381, 449
methyl juloline, 552	Lepidine, 546
Ketone carboxylic acids, 28, 238, 257	Lepidone, 548
derivatives of dibenzyl, 371	Leucaniline, 352, 353
tricarboxylic acid, 266	Leucaurines, 359, 360
oxybiazolines, 516	Leucine, 253
Ketones, 380, 383, 407, 466	Leucobenzaurine, 359
Ketonic acids, 466	benzelne, 359
pentamethylene, 26	crystal violet, 358
carboxylic ester, 28	derivatives, 352
phenyl-methyl-pyrazolon, 488	malachite-green, 352
paraconic ester, 264	Leuconic acid, 27, 171
p yraz olidine, 480	rosolic acids, 359, 360
pyrrolidines, 462	thionine, 584
tetrahydroglyoxalines, 499	Licareol, 310
isoquinoline, 557	Lichen substances, 433
naphthalene, 412	Light oil, 49
oxazole, 503	Ligustrum vulgare, 430
pyrimidines, 589	Lilole compounds, 552
quinazolines, 591	Limet oil, 310
Ketoxy-hydroindol, 471	Limonene, 308, 310, 311
11—54	
J 7	

Melilotic acid, 226, 280

Mellimide, 247 Mellithyl alcohol, 177

Melilotus officinalis, 280, 281

methyl ether, 280

Limonene hydrochlo nitroso chl tetrabromi	oride, 311
Limonetrite, 316	
Linalool, 309, 310	
Linaloolene, 309 Liquidambar orienta	lie on t
Litmus, 162, 433	125, 2/1
Lophine, 497, 498	
Lupetidines, 540	
Lupinus luteus, 253	
Luteolin, 228, 433	
Lutidine dicarboxylic	acid, 537
Lutidines, 532	
Lutidinic acid, 537	
Lutidone, 534	ic acid, 538
Lysene, 144	ic acid, 536
Lysidine, 499	
_,, 499	
	1 .
MACI oil, 270	₹ .
MACI oil, 270 Maclurin, 232, 433	
MACI oil, 270 Maclurin, 232, 433 tannic acid	
MACI oil, 270 Maclurin, 232, 433 tannic acid Madder lakes, 427	
MACI oil, 270 Maclurin, 232, 433 tannic acid Madder lakes, 427 Magdala red, 603	, 228
MACI oil, 270 Maclurin, 232, 433 tannic acid Madder lakes, 427 Magdala red, 603 Magnesium diphenyl	, 228
MACI oil, 270 Maclurin, 232, 433 tannic acid Madder lakes, 427 Magdala red, 603 Magnesium diphenyl Malachite-green, 78,	, 228
MACI oil, 270 Maclurin, 232, 433 tannic acid Madder lakes, 427 Magdala red, 603 Magnesium diphenyl Malachite-green, 78, MaleIc acid, 45	, 228 , 133 351, 352, 354, 355
MACI oil, 270 Maclurin, 232, 433 tannic acid Madder lakes, 427 Magdala red, 603 Magnesium diphenyl Malachite-green, 78,	, 228 , 133 351, 352, 354, 355
MACI oil, 270 Maclurin, 232, 433 tannic acid Madder lakes, 427 Magdala red, 603 Magnesium diphenyl Malachite-green, 78, MaleIc acid, 45 hydrazi MaleInanil, 91 phenylhydrazi	, 228 , 133 351, 352, 354, 355 ne, 586
MACI oil, 270 Maclurin, 232, 433 tannic acid Madder lakes, 427 Magdala red, 603 Magnesium diphenyl Malachite-green, 78, Maleïc acid, 45 hydrazi Maleïnanil, 91 phenylhydrazi Malic acid, 464	, 228 , 133 351, 352, 354, 355 ne, 586
MACI oil, 270 Maclurin, 232, 433 tannic acid Madder lakes, 427 Magdala red, 603 Magnesium diphenyl Malachite-green, 78, MaleIc acid, 45 hydrazi MaleInanil, 91 phenylhydrazi Malic acid, 464 Malonanilic acid, 91	, 228 , 133 351, 352, 354, 355 ne, 586
MACI oil, 270 Maclurin, 232, 433 tannic acid Madder lakes, 427 Magdala red, 603 Magnesium diphenyl Malachite-green, 78, MaleIc acid, 45 hydrazi MaleInanil, 91 phenylhydrazi Malic acid, 464 Malonanilic acid, 91 anilide, 91	, 228 , 133 351, 352, 354, 355 ne, 586
MACI oil, 270 Maclurin, 232, 433 tannic acid Madder lakes, 427 Magdala red, 603 Magnesium diphenyl Malachite-green, 78, MaleIc acid, 45 phenylhydrazi Malic acid, 464 Malonanilic acid, 91 anilide, 91 Malonic acid, 442	, 228 , 133 351, 352, 354, 355 ne, 586 l, 129
MACI oil, 270 Maclurin, 232, 433 tannic acid Madder lakes, 427 Magdala red, 603 Magnesium diphenyl Malachite-green, 78, Maleïc acid, 45 hydrazi Maleïnanil, 91 phenylhydrazi Malic acid, 464 Malonanilic acid, 91 anilide, 91 Malonic acid, 442 Malonyl hydrazine, 4	, 228 , 133 351, 352, 354, 355 ne, 586 l, 129
MACI oil, 270 Maclurin, 232, 433 tannic acid Madder lakes, 427 Magdala red, 603 Magnesium diphenyl Malachite-green, 78, Maleïc acid, 45 hydrazi Maleïnanil, 91 phenylhydrazi Malonanilic acid, 91 anilide, 91 Malonic acid, 442 Malonyl hydrazine, 4 phenylhydrazine, 4	, 228 , 133 351, 352, 354, 355 ne, 586 l, 129
MACI oil, 270 Maclurin, 232, 433 tannic acid Madder lakes, 427 Magdala red, 603 Magnesium diphenyl Malachite-green, 78, Maleïc acid, 45 hydrazi Maleïnanil, 91 phenylhydrazi Malonanilic acid, 91 anilide, 91 Malonic acid, 442 Malonyl hydrazine, 4 phenylhydrazine, 4	, 228 , 133 351, 352, 354, 355 ne, 586 l, 129 191 zide, 129 Izide, 129

Mandelic acid, 251, 257

Mandelnitriloglycoside, 430

Mannitol hexabenzoate, 198

Maringa tannic acid, 228 Martius yellow, 401, 402

Mateza roritina, 295

Matezite, 295 Matricaria camphor, 327

Mauvaniline, 356

Meconic acid, 523

Mauveine, 603

Meconine, 235

Melaniline, 88

Mandelo-nitrile diglucose, 430

nitrile, 251

chloralide, 251

acetic acid, 264

hydrocotarnine, 577

Mellitic acid, 43, 57, 191, 246 Mellophanic acid, 56, 246 Menaphthylamines, 407 Mentha camphor, 308, 313 diene alcohols, 317 dien ketones, 320 Menthan, 309 bases, 317 group, 310 Mentha piperita, 313 pulegium, 320 Menthene, 293, 309, 313 alcohols, 316 bases, 317 glycol, 315 Menthoamide, 318 Menthoic acid, 318 Menthol, 313, 318 Menthomenthene, 313 naphthene, 313 Menthone, 292, 296, 308, 318 nitrile, 318 Menthoxime, 318 Menthylamine, 317 chloride, 314 Mercaptans, 156 Mercapto-methyl penthiazoline, 583 thiazole carboxylic ester, 506 thiazoles, 505 triazole, 512 Mercury dialphyls, 133 phenyl, 133 thiophenate, 157 Mesicerine, 233 Mesidic acid, 55, 242 Mesidine, 76 hydroiodide, 72 Mesitene lactam, 534 Mesitol, 144 Mesityl alcohol, 177 amine, 179 Mesitylene, 50, 53, 55 glycerol, 233 glycol, 232 Mesitylenic acid, 55, 195 Mesityl glyoxylic acid, 259 isophthalic acid, 243 Mesorcin, 161, 162 Meta-compounds, 35 diazines, 587 dioxyanthraquinone, 428 hemipinic acid, 242 anhydride, 242

Metanilic acid, 137 Metaphthalophenone, 351 thiazine, 582 Metazines, 580 Methenylamidophenol, 504 thiophenyl, 89 diphenyldiamine, 83 piperazine, 594 Methoxy-amidoquinoline, 547 benzaldehyde, 219 benzyl alcohol, 217 malonic acid, 262 cinnamic acid, 280 indol carboxylic acid, 470 isatin, 470 Methoxyl-coniferine, 430 Methoxymandelic acid, 252 methyl-quinoline, 548 oxybenzaldehyde, 220 cinnamic acid, 283 phthalaldehydic acid, 237 styrone, 272 phenylglyoxylic acid, 259 methacrylic acid, 282 phthalide, 236, 237 pyridine, 534 quinaldine, 549 quinolinic acid, 537 quinone, 170 tetrahydroquinoline, 551 Methronic acid, 451 Methyl acetanilide, 82 acetyl cyclohexanone, 319 hexamethylenecarboxylic ester, 302, 307 acridine, 560 acridone, 560 adipic acid, 314 alizarin, 428 amido-chlorstyrene, 466 diphenyl thiazoline, 507 thiazole, 505 thiophenol, 507 triazsulpholes, 518 aniline, **78,** 83 anthracene, 422 quinone, 423, 425 antipyrine, 489 arbutin, 429 Methylated diphenyl phthalides, 363 atropic acid, 279 benzamide, 199 benzene-azo-methyl amidobenzene, 114 benzidine, 338 benzimidazole, 500 benzoic ester, 198 benzoln, 372 paroxazine, 581

Methylbenzothiazole, 157, 507 benzoxazole, 153, 503, 504 benzoyl-acetic ester, 260 benzyl chloride, 177 cyanide, 203 isoxazolon, 495 malonic acid, 262 Methyl-brom-pyrazole, 483 carbazole, 477 carbostyril, 84, 548 carboxyanthranilic ester, 212 cetyl benzene, 57 chavicol, 269 chlorphthalazone, 586 quinoline, 547 stilbene, 375 cinchoninic acid, 549 cinnamic acid, 278 aldehyde, 272 coumaric acid, 282 coumarilic acid, 464 coumarin, 279, 282 coumarone, 146, 464 cumar-alcohol, 271 ketone, 273 cyclohexane, 292 pentanol, 26 pentanon, 26 pentenon, 26 desoxybenzoln, 371 dibenzamide, 200 bromoxyphthalic acid, 434 ethyl pyrazine, 593 hydro-diphenyl quinoxaline, 596 isoquinoline, 557 quinazoline, 590 quinoline, 555 resorcinol, 297 ketohydrindene, 388 carboxylic ester, methyl penthiazoline, 583 oxpyridine, 535 oxycyanidine, 605 naphthoquinone, 405 phenylamine, 80 glyoxalidine, 498 Methylene blue, 95, 158, 443, 580, 584 coumarilic ester, 464 dibenzyl ether, 177 dimethyl apionol, 166 oxybenzyl glycol, 248 cinnamyl formic acid, 287 isoquinoline, 555, 578 phenylethylene methyl gly-<u>-col, 248</u> phenyl-diamine, 💋 -phenylene oxide, 524 sulphide, 526

~~~	
Methylene-diphenyl thiourea, 446	Methylisoformanilide, 82
pyrocatechol, 343	indol, 463
metahemipinic ether acid, 242	phthalic acid, 242
methyl gallic ether acid, 230	propyl benzenes, 56
phthalide, 285	cyclohexane, 292
dibromide, 285	diphenylenemethane, 41
phthalimidine derivatives, 286	hexahydrophenol, 313
protocatechuic acid, 228	ketohexamethylene, 296
thiourea, 446	hexene, 298
ur <b>ea, 44</b> 6	carboxylic
Methyl-ethyl-acetic acid, 431	ester, 30
aniline, 78	phenanthrene, 415, 416
ethyl iodide, 78	phenol, 144
furazane, 515	pyrrol, 459
glyoxaline, 498	succino-succinic ester, 30
isoxazolon, 495	tetrahydrobenzene, 293
pyridine, 528, 532	quinoline, 556
thetine, 446	isoxazole, 494
thiobetaine, 446	isoxazolon, 494
eugenol, 269	ketodihydro-methyl quinoxaline,
fluorindene, 603	596
formanilide, 82	quinazoline, 591
furazane carboxylic acid, 515	hexamethylenes, 296
furfurane, 448	hexene, 298
acetic carboxylic acid,	carboxylic ester, 302
451	307
furfurol, 450	ketol, 124, 467
gluco-cumar-ketone, 430	mercapto-thiazole, 506
glyoxalidine, 499	triazole, 512
glyoxaline, 497	morphimethine, 576
phenyl hydrazoxime, 124	morphine, 576
granatoline, 571	naphthalene, 394
green, 358	naphthol, 391, 400
heptenone, 310 hexahydrofluorene, 418	naphtho-phenazonium iodide, 600
methylene dicarboxylic ester,	nicotinic acid, 536
	nitropyrazole, 483 noropianic acid, 237
302 methyl ketone,	opianic ester, 237
302	oxazoline, 503
hexyl-keto-hexene, 298	oxindol, 468
homo-oxybenzoic acid, 226	oxyquinoline, 544, 548, 596
salicylic acid, 226	thiazole, 505
hydrindone, 387	paraconic acid, 391
hydrocotoin, 349	pelletierine, 571
quinone, 163	penthiophene, 438
idene carboxylic acid, 383	phenanthridine, 558
imidohydrocinnamic ester, 260	thridinium iodide, 558
indazole, 492	thridone, 558
indene, 383	throline, 554
carboxylic acid, 386	pheno-stilbazonium hydroxide, 59
indol, 466, 467	phenpenthiazole, 181, 583
acetic acid, 127	pentoxazole, 181
carboxylic acid, 468	phenyl ether, 146
sulphonic acid, 468	furfurane-carboxylic acid
isatin, 259, 472	451
tolylimide, 259	hydrazine, 121
isobutyl-keto-hexene, 298	hydrazone acetoacetic ester
carbostyril, 286, 556	\ 468
coumarin, 286	iso-crotonic acid, 278
· · · · · · · · · · · · · · · · · · ·	

	243
Mathul phonul itaconia said alla	Mathal thiogham
Methyl-phenyl itaconic acid, 289	Methyl thiophene, 454
methane, 351	tolimidazole, 501
oxazole, 503	tolylthiazoline, 506
oxazoline, 503	triazole, 512
paraconic acid, 263	methylene, 22
phthalazone, 238	phenyl dioxazine, 582
propiolic acid, 285	methane carboxylic acids,
pyrrol, 459	362
quinazoline, 589	umbelliferone, 283
quinoline, 347	vinyl-piperidene, 540
sulphone, 139	violet, 357, 358
thiocarbamin chloride, 87	Metoxazine group, 439
urea chloride, 85	Middle oil, 49
phthalazone, 238, 587	Mimosa catechu, 159
phthalide, 235	Mixed azo-bodies, 112
phthalimide, 241	compounds, 113
pipecolyl alkine, 540	Monacet-diamido-diphenylamine, 118
piperazine, 594	acetyl-dioxyphenanthrene, 415
piperic acid, 285	acid menthan alcohols, 313
piperidine, 540	amido-phenazine, 599
protocatechuic acid, 228	Monarda punctata, 144
purpuroxanthins, 428	Monoalkylamido-phenols, 154
pyrazine, 593	brom anthraquinone, 425
pyrazole, 480, 482	cinnamic aldehyde, 272
carboxylic acid, 485	hexahydrobenzoic acid, 300
sulphonic acid, 483	toluic acid, 300
pyrazolon, 487	methylene phthalide, 285
pyridazinone, 585	quinone, 163
pyridine carboxylic acid, 536	stilbene, 375
dicarboxylic acid, 537	chlorcinnamic aldehyde, 272
pyridines, 532	quinone, 163
pyrogalloldiethyl ether, 164	stilbene, 375
methyl ether, 164	halogen anthracenes, 423
mucic acid, 451	heteroatomic five-membered rings,
pyrrol, 458	447
carboxylic acid, 461	four-membered rings,
pyrrolidine, 462	446
carboxylic acid, 462	three-membered rings,
pyrroline, 461	444
quinaldone, 549	hydric phenyl-paraffin alcohols, 176
quinazoline, 187, 589	ketazocamphor-quinone, 330
quinoline, 542, 545	nitroquinone, 425
carboxylic acid, 549	nitrosonaphthalene, 396
quinolinic acid, 537	terephthalic acid, 243
quinoquinoline, 554	phloreticphloroglucin ester, 226
salicyl chloride, 224	thiopyrocatechol, 160
selenazoline, 508	Monoxyalcohol acids, 250
styrolene, 268	anthracene, 423
sulphonic phenyl ester, 147	quinones, 426
terephthalic acid, 243	benzaldehydes, 218
tetrahydrobenzene, 293	benzoic acids, 222
isoquinoline, 557	benzyl alcohols, 217
quinoline, 551	phenyldiphenyl tetrazolium chlo-
thiazole, 504	ride, 521
carboxylic acid, 506	olefine carboxylic acids, 279
dicarboxylic acid, 506	pyridine, 534
thiazoline, 506	carboxylic acid, 537
thiazylacetic ester, 506	triphenyl methanes, 359
thioacetanilide, 83	Monthiohydroquinone, 164
• •	•

Mordant dye, 405 Morin, 232 Morinda citrifolia, 427 Morindin, 427 Moringa tannic acid, 159 tannin, 232 Morphine, 576 Morpholine, 581 thebaine, 576 Muscat nut oil, 270 Mustard oil, 83, 97, 269 acetic acid, 507 Myrcene, 309 Myricetin, 524 Myristicine, 270 Myristicinic acid, 230 Myronic acid, 429 Myrosin, 429 N. NAPHANTHRACENE, 429 Naphanthraquinone, 429 Naphsultamdisulphonic acid, 399 Naphsultone, 403 Naphthacetin, 401 Naphthacetol, 401 Naphthaldehyde, 407 Naphthaldehydic acid, 410 Naphthalene, 48, 67, 384, 392, 394 azo compounds, 138, 397 diazo-oxide, 516 carboxylic acid, 409 chloride, 411 sulphonic acids, 394, 398 disulphydrates, 404 group, 389 homologues, 394 monocarboxylic acids, 408 poly-carboxylic acids, 409 red, 398 ring formations, 390 sulphinic acids, 400 sulphonic acids, 398 tetrabromide, 411 carboxylic acid, 409 chloride, 411 trisulphonic acids, 398

yellow, 401, 403
Naphthalic acid, 405, 409
Naphthalidinic acid, 399
Naphthalizarin, 405
Naphthazarin, 396
Naphthazarine, 405, 426
Naphthazine, 598
Naphthenic, 291, 300
Naphthenic acids, 300
Naphthindulines, 602

Naphthinoline, 558 Naphthionic acid, 399 Naphthoazimides, 397 benzyl alcohols, 407 amines, 407 chlorides, 407 cyaminate, 396 derivatives of heterocyclic rings diphenyl-dihydrotriazine, 606 furazane, 407, 515 furfurane, 464 Naphthoic acid, 408 ketocoumaran, 464 Naphthol, 391, 392, 400, 464 Naphthol, alkyl ethers, 400 azobenzene, 401, 402 black, 400 blue, 407, 582 carboxylic acids, 408 diazobenzene, 401 sulphonic acids, 402 ethyl ether, 400 green, 406 homologues, 400 methyl ether, 400 ketone, 407 monosulphonic acids, 402 orange, 402 Naphthols, 400 Naphthol sulphonic acids, 402, 406 trisulphonic acids, 403 yellow, 401, 403 Naphthomethylfurfurane carboxylic ester 464 nitriles, 409 phenazine oxide, 600 phenazines, 398 ocarbazole, 478 osafranine chloride, 603 oxazine, 582, 598 oxazone, 582 quinoline, 531, 553 quinone, 393, 405 anils, 407 carboxylic acid, 400 chlorimides, 407 dichloriimide, 407 oxime, 406 imides, 407 phenyldiimide, 407 hydrazones, 406 quinones, 402, 404 quinoxalines, 595 quinoximes, 406 resorcinol, 404 styril, 408

Naphthoxanthones, 408

Naphthoxazoles, 401

```
Naphthoxylacetaldehyde, 464
Naphthyl-acetic acid, 407, 408
          acetylene, 407
          amido-thiobiazolon, 517
                 thio-oxybiazoline, 516
          amine, 391
                   azo-benzene sulphonic
                     acid, 398
                   disulphonic acids, 399
                   sulphonic acids, 399
          amines, 396, 468
                  acid derivatives of, 397
          azoacetic acid, 398
                   ester, 398
          benzene sulphamides, 397
          blue, 602
          carbamine chlorethyl esters, 397
          carbinols, 407
          dimethylamine, 396
Naphthylene diamines, 397
              diamine sulphonic acid, 399
              oxamide, 596
              phenylene methane, 418
Naphthylenes, 293
ethylamine, 396
         hydrazines, 398
          indigo, 475
          indol, 468
         iodo-chlorides, 395
         mercaptan, 404
         methylamine, 396
                 ketone, 407
          naphthoic acids, 408
         phenylhydrazone, 468
         piperidine, 540
         sulphones, 400
          violet, 602
Naphthyridine, 558
Naphtidine, 397, 398
Naphtidines, 410
Naphtrisultamsulphonic acid, 399
Narceine, 578
Narcotine, 241, 575, 577
Naringenin, 432
Naringin, 430, 432
Natural dyes, 433
         isocinnamic acid, 274, 276
Neroline, 400
Neutral red, 599
Neville and Winther's acid, 402
New Victoria green, 355
Nicotine, 462, 565
Nicotinic acid, 536
                methyl betaine, 565
Nile blue, 582
Nitranilic acid, 170
Nitranilide, 98
Nitraniline-p-sulphonic acid, 67
Nitranilines, 92
```

```
Nitriles of aromatic monobasic acids, 201
        of phthalic acid, 241
Nitroacetophenone, 190, 284, 474
     alizarin, 427, 428
     amido cinnamic acid, 278
            diphenyl, 337
           nicotinic acid, 533, 536
            tetraoxybenzene, 166
     amines, 63, 80
     anilines, 67
     azobenzene, 113
     benzal acetone, 273
     benzaldehyde, 186
                    oxime, 186
                    hydrazone, 186
           malonic acid, 288
     benzazides, 201
    benzene, 75
              azo-amido-benzene, 115
             diazoxyamido-methane, 110
    benzenes, 66
     benzidine, 337
     benzmalonic ester, 262
     benzoic acid, 210
          nitrile, 210
          phenone, 347
     benzoyl-acetic acid, 260
             acetoacetic ester, 262
             acetone, 250
             formic acid, 258
                         amide, 258
                         nitrile, 258
                         oxime, 258
phenylhydra-
                            zones, 258
             malonic ester, 263
     benzyl alcohol, 180
            amine, 181
            aniline, 181
            chloride, 180
            cyanides, 211
            formamide, 181
            malonic acid, 469
            nitrobenzaldoxime, 187
            nitrobenzene, 343
            phenyl nitrosamine, 181
            sulphocyanide, 180
     bromacetophenones, 249
          benzaldehyde, 187
          hydrocinnamic acid, 254, 255
     carbazole, 477
    carbostyril, 548
chlorbenzaldehyde, 187
          methyl phthalide, 393
          styrolene, 268
     cinnamenyl acrolein, 272
     cinnamic acid, 277, 465, 474
              aldehyde, 272
               ethyl ester, 277
```

Nitrococcic acid, 226, 433 compounds, 31, 63 coumaric acid, 279, 280, 281 coumarinic dimethyl ether, 281 cresols, 151 desoxybenzoln, 371 diamido-diphenyl, 337
triphenyl methane, 352 azobenzene acids, 99
imide, III
phenol, 516
bromhydrocinnamic acid, 256
ethyl ester,
256
methyl aniline, 78 phenyl, 336
amines, 80, 92
amine-suboxide, 584
disulphides, 137
methane, 343
ethoxy benzonitrile, 67
formyl hydrazide, 120
furfurane, 448
Nitrogen derivatives of the naphthoqui- nones, 406
haloid benzenes, 67
benzoic acids, 210
hydratropic acids, 211
hydrazo-benzenes, 117
hydrocinnamic acids, 211
quinone, 164
indazole, 492, 493 iodanisol, 151
isophthalic acid, 242 quinoline, 555
malachite greens, 355
mandelic acid, 251
mesitylenes, 68
methylcinnamic aldehyde, 385
indazole, 493
mono-carboxylic acids, 210
naphthalene-diazo-oxide, 516
sulphonic acids, 399 naphthalenes, 395
naphthoic acids, 408
naphthol, 401
naphthols. 401
naphthoquinone, 393, 406
naphthylamines, 397
opianic acid, 238
oxanilic acid, 91
oxypyridines, 533 phenanthrenes, 414
phenol, 150
phenols, 149
phenyl acetaldehyde, 465
acetic acids, 210
acetylene, 268
alanine, 253

```
Nitrophenyl benzoic acid, 340
              bromlactic acid, 256
              chloriactic acid, 256
              diazomercaptan hydrosul-
                phide, 103
hydroIndazole-carboxylic
                   acid, 493
              ether, 146
              glyceric acid, 255
              glycidic acid, 255, 256
              glycin, 84
              hydracrylic acid, 254
              hydrazine, 120
              indazolon, 493
isindazole carboxylic acid, 493
              lactic acid, 253, 254
                           aldehydes, 248
                           ketones, 249
                           lactones, 254
                           methyl ketone.
                              474
              methyl pyrazolon, 488
              naphthalene, 395
nitroacrylic acid, 253, 278
              propiolic acid, 284, 471
                              ethyl ester, 284
                        ester, 469
              pyridine, 532
              pyroracemic acid, 468, 470
              quinoline, 546
      phthalic acids, 241
     phthalide, 235
prehnitol, 68
      pyrazole, 483
      pyrazoles, 483
      pyridines, 533
      pyromucic acid, 451
     quinolines, 547
     quinone, 169
salicylic acid, 225, 472
Nitrosamines, 63, 78, 80
Nitrosites, 267, 270
Nitrosoacetanilide, 98
        alkylamines, 151
        alphyl-hydroxylamines, 70
        anilides, 83, 98
        aniline, 94
anthrol, 423
        antipyrine, 489
benzaldehyde, 187
        benzene, 70
                  sulphonic acid, 137
     · benzoic acid, 211
        carbazole, 477
        compounds, 78
        conine, 564
        cresol, 152
        derivatives, 69, 93
dimethyl anilime, 78, 94
```

Nitrosodiphenylamine, 80, 94	Oil of absinthe, 319
ethylamido-cinnamic acid, 277	of bergamot, 311
formanilide, 98	of bitter almonds, 430
hydrazines, 63	of cassia, 272
hydroxylamines, 63	of celery, 311
indazole, 492	of cumin, 320
indol, 466	of dill, 311
mono-carboxylic acids, 211	of garlic, 268
naphthalenes, 396	of lavender, 310
naphthol, 400	of lemons, 310
naphthoquinone oxime,	of Matricaria parthenium, 327
406	Olefine benzenes, 266
naphthols, 406	dioxybenzenes, 269
sulphonic acid, 406	monoxybenzenes, 269
orcin, 162	phenols, 268
phenol, 151, 152, 168	terpenes, 308
phenols, 151	tetraoxybenzenes, 270
phenylglycin ester, 126	trioxybenzenes, 270
semicarbazide, 131	Olefinic terpene acids, 310
phloroglucin diethyl ether, 165	alcohols, 309
phthalimidine, 234	aldehydes, 310
pinene, 323	group, 309
piperidine, 540	Oleum cina, 311, 315
tetrahydroquinoline, 550	Olive soaps, 144
thymol, 152	Opianic acid, 235, 237
toluene, 70	Opianoximic acid, 237
Nitrostyrolene, 254, 267	anhydride, 237
thiophene, 454	Opium bases, 575
toluenes, 68	Orcendialdehyde, 233
trimethyl-pyrazole, 483	Orcin, 161, 162
phenylcarbinol, 353	aurine, 361
methane, 351	Orcinol, 161
xylene, 68	Orcins, 366
Nonaphthene, 292	Orcirufin, 582
Nopic acid, 301, 323	Origanum, 310
Norhemipinic acid, 241	Orpholum, 400
Normal diazohydrates, 102	Orsellic acid, 162, 229
Normeconine-acetic acid, 264	Ortho-benzoic acid piperidide, 209
Normetahemipinic anhydride, 242	compounds, 35
Noropianic acid, 237	diazines, 584
Norpinic acid, 323	phosphor anilide, 80
Nucleus acidylated alkyl benzenes, 190	phthalophenone, 351
syntheses, 19	quinones, 167
synthetic, 257	thiazines, 582
reactions, 50	Orthoxazine group, 439
	Orthoxazines, 580
	Osazone, 387
О.	Osazones, 122
	Osobenzene, 48
OAK-RED, 232	tetrazones, 124, 131, 442, 606 triazine derivatives, 442
Octadecyl benzene, 57 Octochloracetylacetone, 46	
ketotetrahydrobenzene, 298	triazole, 479, 508 carboxylic acid, 509
hydrocarbostyril, 300	
naphthalene, 413	group, 441 triazoles, 124, <b>508</b>
naphthalene, 413	Oxaldiamidoxime, 130
naphthyridine, 558	enbisazoximethenyl, 515
naphthene, 292	Oxalic acid, 393, 441
Octyl benzene, 57	Oxalimide, 438, 440, 444
11—55	Commerce of Jan days dad

•	
Oxalines, 496	Oxydihydroquinoxaline, 595
phenylhydrazide, 129	methyl benzenes, 144
hydrazilic acid, 129	phenyl amine, 154
Oxalylanthranilic acid, 212	phenylene ketone, 419
diacetone, 494	triazine, 374
acetophenone, 383	ethyl benzenes, 144
guanidine, 499	benzoic acid lactone, 235
urea, 499	fluorene carboxylic acid, 419
Oxanildioxime, 91	fluorenone, 419
anilic acid, 90	furazane carboxylic acid, 515
anilide, 89, 91, 374	hexahydro-cymene, 313
anthranol, 425	isophthalic acid, 304
atolylic acid, 380	methylene carboxylic acid, 301
azines, 580	hydratropic acid, 226
azole group, 439, 441	hydrindene, 387
azoles, 373, 479, 480, 502	hydrobenzene dicarboxylic acid, 304
azolines, 503	carbostyril, 253, 254, 551
ethyl-amidophenol, 152	quinone, 165
anisidine, 153	tri-ethyl ether, 165
ime anhydrides, 259	methyl ether, 166
imido-propiophenone, 250	indol, 468
indol, 214, 465, 471	carboxylic acid, 262, 468, 470
Oxodihydrobenzenes, 149	isophthalic acid, 243
cumaein, 259	propyl benzoic acid, 236
menthylic acid, 314	lactone, 235
tetrahydrobenzenes, 149	quinolines, 556
Oxyacetophenone, 221	juglone, 405
anthraquinones, 426	mandelic acid, 252
antipyrine, 489	lactone, 252
azobenzenes, 155	mesitylenic acids, 226
benzal acetone, 273	methylbenzoic acid, 233, 234, 235, 251
benzoic acid, 222	lactone, 234
phenone, 348	coumarin, 283
thiazole, 157, 508	methylene acetophenone, 287
thiophene, 465	camphor, 330
benzoxazole, 153, 504	anhydride, 330
benzyl alcohol, 217	cyanhydrin, 330
amine, 217	compounds, 256
benzenes, 343 idene acetophenone, 379, 383	menthone, 318 phenyl acetic ester, 287
biazole group, 441	ethyl ester,
azoles, 479, 480, 516	257
azoline derivatives, 126	methylquinoline, 548
azolon derivatives, 127	tetrahydroquinoline, 551
phenyl carboxylic acids, 340	thiazole carboxylic ester, 506
phenyls, 339	thiophene, 455
camphenilanic acid, 322	tolimidazole, 501
camphor, 329	naphthoic acid, 394, 408
carbostyril, 548	naphtho phenazine, 600
chlorstyrene, 463, 464	quinone, 405
styrolene, 269	anil, 405, 407
chrysazin, 428	oxime, 407
cinnamic acid, 280	naphthylamine, 396
cinnamylidene acetic acid, 287	nicotinic acid, 537
cinnoline carboxylic acid, 586	pentacarboxylic acid, 265
coumarin, 283	decylic acid, 421
cyclopentan carboxylic acid, 27	phenazines, 600
diamido-cyanidine, 605	oxazime, 582
triphenyl methanes, 359	oxazine, 153

	•
)xyphenoxazone, 582	Oxytrimellitic acid, 246
thiazone, 584	mesic acid, 246
phenylacetic acid, 226	methyl piperidines, 540
lactone, 227	phenyl methane, 359
acetonitrile, 226	carboxylic acids,
alanine, 253	362
benzoic acid, 340	uvitic acid, 243
ethylamine, 217, 254	xanthone, 524
glyoxylic acid, 259	xanthones, 525
indazole, 493	
lactic acid, 253	
methyl pyrazolon, 488	P.
pyridazone, 585	= -
mustard oil, 153	PÆNOL, 22I
olefine alcohols, 271	Palmityl benzenc, 190
aldehydes, 272	Papaveraldine, 576
carboxylic acids, 279	Papaveraline, 576
ketones, 273 phthalide, 349	Papaverine, 576 Para-anthracene, 422
propionic acid lactone, 227	azines, 581
acids, 226	banic acid, 499
pyroracemic acid, 259	camphoric acid, 332
succinic acid, 262, 281	compounds, 35
thiourea, 153	coto bark, 349
urea, 153	oil, 270
phosphazobenzene anilide, 80	diazine, 592
phthalic acid anhydride, 241	dyes, 405
acids, 241	glyoxal methylin, 498
phthalide, 235	leucaniline, 352, 357
picolinic acid, 537	mandelic acid, 251
picric acid, 161	derivatives of, 251
pipitzaholc acid, 170	Paramide, 247
pyrazoles, 483	oxybenzoic acid, 254
pyridine carboxylic acids, 537	quinones, 167
dicarboxylic acid, 537	rosaniline, 353, 356
pyridines, 522, 533	constitution of, 356
pyridone, 534	rosolic acids, 361
pyrone, 522	thiazine, 443, 583
carboxylic acid, 523 pyrrodiazole dicarboxylic acid, 510	group, 442
quinaldine, 85, 548	Paroxazine, 443
carboxylic acid, 213	dyes, 405 group, 439, 442
quinazoline, 591	Parsley seeds, 271
quinoline carboxylic acids, 550	Parvuline, 532
quinolines, 547	Pelargonium oil, 309
quinolinic acid, 537	Pelletierine, 571
quinone homologues, 170	Penicillium glaucum, 251
quinones, 170	Pentaamidocyclopentadein, 172
quinoxaline, 596	phenol, 172
suberanic acid, 29	toluene, 97
terephthalic acids, 243	bromaniline, 92
terpenylic acid, 320	diketo-oxy-hexene hydrate, 297
thionsphthene, 465	toluene, 292
phene, 455	carbocyclic compounds, 25
tolene, 455	chloraniline, 92
thymoquinone, 170	diketo-hexene, 299
toluenes, 143, 144	naphthalene, 395
toluic acids, 225 tricarboxylic acids, 246, 2 <b>6</b> 5	orcin, 162
a car boxyric acids, 240, 205	phenol, 298

052	BA.
Describbenesiding too	Phononthroquinone managime 425
Pentachlorpyridine, 533	Phenanthraquinone monoxime, 415
resorcinol, 46	anthrene, 48, 384, 413, 414
xylene, 237, 250	carboxylic acids, 414
hydric phenols, 166	dibromide, 414
ketocyclopentane, 171	group, 413
pentamethylene, 27	hydroquinone, 415
methyl benzene, 56	octo-chloride, 414
benzoic acid, 196	sulphonic acids, 414
diphenyl methane, 343	tetrahydride, 414
methylene, 25	anthridine, 557
imide, 442, 538	anthridone, 558
piperidine, 438	anthrofurazane, 515
oxide, 437, 442	anthroline, 545
methyl phenol, 145	anthrone, 415
triamidotriphenylmethane,	anthrophenazine, 598
358	ales, 143
violet, 358	azine, 160, 215
Pentamines, 97	group, 597
phenylpyridine, 383, 529	azone, 337, 587
pyridines, 533	benzyl dihydro-triazine, 606
Penthiazoline group, 442	diol, 159
Penthiophen, 525	Phene, 47
Penthiophene group, 442	l'henethyl benzyl ketone, 380
Pentol, 25	Phenetidine, 154
l'entosides, 429, 431	l'henetol, 146
Pentoxazoline, 439	carbamide, 154
group, 442	keto-dihydro-triazine, 606
Peonine, 361	methyl dihydrotetrazine, 122
Peppermint oil, 313, 318	metadiazine, 187
Perchloracetoacrylic acid, 46	methylol, 176
acroyl acrylic acid, 45	triazine, 605
diphenyl, 336	morpholine, 153
indone, 27, 386, 387	Phenol, 45, 142, 171, 174, 464
naphthalene, 394, 395	alcohol-ethers, 145
pentene, 25	alcohols, 217
pyrocoll, 461	aldehydes, 218
trimethyl cyanidine, 604	ates, 143
vinyl acrylic acid, 45	benzeīnes, 360
Peri-naphthalene derivatives, 409	derivatives of triphenyl carbinol,
Perkin's reaction, 273, 277	360
Pernitroso camphor, 330	methanes,
Persea cassia, oil of, 272	359
Persea cinnamomum, 272	diazobenzene, 155
Persio, 162	ohlorides, 154
Peru balsam, 274	mercaptan hydrosulphide
Pesacetophenone diethyl ether, 221	155
Petroselinum sativum, 271	disulphonic acid, 156
Phaseolus vulgaris, 295	ethers, 146
l'haseomannite, 295	ethylene ether, 146
Phellandrene, 312	glyoxylic acids, 269
nitrosite, 312	ketones, 220
Phellandrium aquaticum, 312	monocarboxylic acids, 221
Phenacetin, 154	naphthalein, 409
Phenacetol, 146	phenylethane, 368
Phenacylacetone, 250	phthalein, 364
anilide, 249	anhydride, 365
chloride, 248	anilide, 364
anthraquinone, 97, 415	oxime, 364
dioxime, 414	phthalol, 361

Phenols, 31, 51, 114, 135, 140, 144, 158, Phenylaldehyde ketones, 249 164, 166 alkylamines, 77 salicylic ester, 224 ammonium bases, 77 sulphonic acid, 156 hydrazines, 121 trisulphonic acid, 156 allophanic ester, 86, 148 Phenomauveine, 603 allyl acetic acid, 279 naphthacridone, 560 nitrile, 279 oxanthones, 525 allylene, 268 quinone, 168 malonic acid, 289 sulphone, 139 safranine, 603 amidoacetic acid, 252 Phenose, 295 oxalkylamines, 146 methyl ester, 252 oxazine, 153, 160, 581 nitrile, 252 oxethylamine, 146 azobenzene-sulphonic acid, oxyacetaldehyde, 146 cinnamic acid, 377 acetals, 464 hydrocinnamic acid, 376 acetic acid, 146 acryl methyl ketones, lactic acid, 256 methylisotriazole, 509 273 acetoacetic ester, 146 pentoxazoline, 580 acetone, 146 propionic acid, 253 butyric acid, 146 quinoline, 547 thiazole, 505 Phenoxylacetal, 464 amine, 71, 74 diphenylphosphine, 132 ammonium bases, 77 phosphazobenzene, 80 Phenoxypropylamine, 146 amphiglyoxime, 249 angelic acid, 278 phenyl dihydro triazine, 181, 606 anthracene, 423 triazine, 206 tetrazines, 442 anthranilic acid, 212 tetrol, 166 anthranol, 424 thiazimes, 584 antiglyoxime, 249 azone, 584, 605 arsenic compounds, 132 thiol, 156 Phenylated carbylamines, 83 triazine, 122, 131, 605 fatty ketones, 189, 190 azyl methyl ketone, 606 pararosanilines, 359 phenylene diamines, 95 Phenylacetaldehyde, 184, 254, 271, 276 acetate, 147 rosanilines, 359 acetic acid, 191, 194, 196 anhydride, 198 ureas, 85 azimidoethoxybenzene, 511 azocarbamide, 103 acetobutyric acid, 261 carboxylic acid, 244 formazyl, 131 acetone, 190 benzaldoxime, 186 aceto-nitrile, 203 sultime, 346 succinic ester, 263 amide, 199 acetyl-acetone, 250 benzene induline, 601 chloride, 198 sulphazide, 119, 125 benzenes, 335 hydrylbenzoic acid, 350 pyrazole, 484 acetylene, 266, 267, 268, 284 carboxylic acid, 284 imidazole, 204, 500 benzoic acid, 340 di-iodide, 267 acridine, 560 ester, 198 acrolein, 272 paroxazine, 581 acrylic acid, 274, 278 thiazole, 199, 204, 507 actazam, 350 benzoxazole, 203, 504 alanine, 84, 253 benzoyl isoxazolon, 495 propionic acid, 377, 380 alcohol aldehydes, 248 dicarboxylic acids, 262 pyrazole, 484 ketone carboxylic acids, urea, 374 261 benzyl-benzoic acid, 350

oso index.	
799 91 4 311 - Sur Arteston and	Thered westers all sections is 90
Phenylketodihydro-triazine, 126	Phenyl mustard oil acetic acid, 88
ketols, 248	Phenylnaphthalene, 394, 395
ketone dicarboxylic acids, 263	naphthoic acid, 408
oxybutyric acid, 261	naphthophenazonium chloride, 600
tetrahydro-oxazole, 503	quinone, 395
tricarboxylic acids, 264	xanthene, 410
lactic acid, 252, 253	naphthylamines, 396
lævulinic acid, 261	carbazole, 478 sulphide, 404
lutidon-carboxylic acid, 85 lutidone carlюxylic acid, 538	nitramines, 98
maleic acid, 289	nitro-ethylene, 267
anhydride, 289	methane, 178
malic acid, 263	paraffins, 178
malonic acid, 262	propylene, 267
ester, 262	nitrosamines, 97
mercaptan, 156	ohydrazine, 131
mercapto-thiazole, 506	ohydroxylamine, 70
mesaconic acid, 289	olefine alcohols, 27I
methyl acetylene, 268	aldehydes, 272
acrylic acid, 278	carboxylic acid, 273
carbinol, 176	acids, 255
chlorpyridazone, 585	keto carboxylic acids, 287
cyantriazole, 509	ketols, 287
dihydrotetrazine, 606	ketone carboxylic acid, 288
ethoxypyrazole, 127, 484	ketones, 272
furfurane, 449	orthoformic ester, 147, 157
glycol, 247	piperazone, 586
oxaline, 503	osotriazole, 509
isoxazole, 494	azimide, 509
ketone, 189	carboxylic acid, 509
methoxypyrazole, 484	dicarboxylic acid, 509
nitramine, 98	oxalacetic ester, 259, 263
nitrosamine, 98	amic-diphenyl-amidine, 91
osotriazole, 509	anthranol, 425
oxazole, 502	azole, 503
oxybiazolon, 516	azoline, 203, 503
osotriazole, 509	oxybenzoic acid, 340
pyrimidine, 205	butyric acid, 255
pentoxazoline, 580	crotonic acid, 287
pyrazole, 124, 481, 482, 483	hydrindone, 387
carboxylic acids,	indol, 470
485	ketone dicarboxylic acids, 264
pyrazolidine, 490	naphthoquinone, 405
pyrazolidone, 490, 491	olefine carboxylic acid, 287
pyrazolon, 127, 481, 487,	phenylpropyl alcohol, 379
488, 489	propionic acid, 252
azobenzene, 488	pyrimidine, 588
pyridazinone, 127, 585	quinoline, 213
pyridazone, 585	carboxylic ester, 544
pyridine, 529, 532	quinoxaline, 596
quinoline, 546	succinic acid, 263
succinic acid, 262	tetrazole, 520
sulphydantoin, 87	thiazole, 505
triazole, 512	thiophene, 261
carboxylic a c i d,	valeric acid, 255
513 triazolon, 128, 513	parabanic acid, 91 paraconic acid, 255, 263
monohaloid acrylic acid, 275	paratin alcohol acids, 250
mustard oil, 89	alcohols, 175
mastaid (iii, by	erconoist r 12

enylparaffin aldehyde carboxylic acids,	
256	rosinduline, 602
dicarboxylic acids, 262	salicylic acid, 340
diketones, 250	selenides, 158
$oldsymbol{eta}$ -ketone carboxylic acid,	selenium hydrate, 158
259	semicarbazide, 86, 127
ketone carboxylic acids,	serin, 256
257	silicates, 147
tricarboxylic acid, 264	silicon compounds, 133
penthiazoline, 204, 583	styrenyl triazolon, 513
pentoxazoline, 203	succinic acid, 262
phenacyl acetic acid, 380	sulphamic acid, 80
anthridine, 558	sulphide, 157
azonium chloride, 600	sulphocarbazinic acid, 128
phenylimido-oxybiazolon, 516	carbizine, 128, 157, 608
phosphine, 132	cyanate, 89
phosphorus compounds, 132	sulphone acetic acid, 139
phthalide, 349	semicarbazide, 128
phthalimidine, 234	ureas, 87
piperic acid, 381	sulphurethane, 86
piperidine, 58, 540	ethanes, 86
propiolic acid, 266, 267, 284	sulphuric acid, 147
ester, 259	tellurides, 158
propionic acid, 197	tetrahydropyramidine, 588
propionitrile, 203	pyrimidine, 204, 205
propyl alcohol, 177	quinazoline, 181, 591,
aldehyde, 184	59 <b>2</b>
amine, 179	tetrazole, 519, 520
propylene thiourea, 507	carboxylic acid, 520
propylidene acetic acid, 278	mercaptan, 520
triazolon, 513	methyl sulphide, 520
pyrazole, 481, 482, 483	tetrazotic acid, 205
carboxylic acid, 485	tetrose, 248, 256
dicarboxylic acids, 485	thiazole, 505
pyrazoles, 483	thiazoline, 204, <b>506</b>
pyrazolidine, 490	thiobiazoline sulphydrate, 517
pyrazolidon-carboxylic acid, 129	biazolon sulphydrate, 128
pyrazolidone, 491	hydantoins, 87
pyrazoline, 481, 485, 486	pentahydrodiazthine, 128, 608
dicarboxylic methyl es-	phene, 454
ter, 486	salicylic acid, 224
pyrazolon, 260, 284, 487	semicarbazide, 88
carboxylic acid, 490	tetrazole, 519
pyridazinone, 585	tetrazoline, 520
carboxylic ester, 585	thiuramsulphide, 87
pyridine, 531, 532	thiurea, 87
dicarboxylic acid, 531	tin compounds, 133
pyridone, 534	tolyl, 336
pyridyl ketone, 535	carbinol, 344
pyrimidone, 588	ketone, 345
carboxylic acid, 588 pyrone, 522	methane, 343 phthalide, 363
pyroracemic acid, 280, 259	propane, 267, 370
pyrrodiazole dicarboxylic acid, 510	triazole, 126, 512
pyrrol, 458, 459	aldehyde, 509
quinaldine, 546	carboxylic acid, 513
quinazoline, 589	dicarboxylic acid, 513
carboxylic acid, 589	triazolon, 513
quinazolon, 347	carboxylic acid, 513

•	
Phenyltribrom-pyrazole, 483	Phthalidacetic acid, 264, 287
carboxylic acid, 485	carboxylic acid, 264
iodethylene, 267	propionic acid, 264
methyl ammonium iodide, 72	Phthalide, 234, 463
	enil coa
pyrazolon, 489	anil, 234
oxybutyric acid, 256	chloride, 234
lactone, 256	Phthalideines, 364
uracil, 260	ideIns, 424
urazole, 127, 128, 514	Phthalides, 362
urea, 85	Phthalidines, 364
bromide, 85	Phthalidins, 424
chloride, 85	imide, 236, 240, 463
urethanes, 85	acetic acid, 289
valeric acid, 197	imidine, 234, 463
valerolactone carboxylic acid, 263	Phthalin, 362
vinylamine, 267, 276	Phthalins, 364
ethyl ether, 271, 287	Phthalone, 501
xylylpropane, 370	Phthalonic acid, 265
Phlobaphene, 232	nitrile, 241
Phloretic acid, 226, 431	phenones, 350
Phloretin, 165, 226, 431	Phthalyl acetic acid, 280
Phloridzin, 430	alcohol, 232
Phlorine, 366	chloride, 240
Phloroglucin, 46, 136, 165, 366, 464	cyanacetic ester, 290
carboxylic acid, 230	diacetic acid, 265
triacetate, 165	malonic acid, 265
carboxylic ester, 246, 306,	ene tetrachloride, 240
307	green, 363
ethyl ether, 165	hydrazine, 241, 587
methyl ether, 165	hydroxamic acid, 241
oxime, 165	phenylhydrazide, 241
glucite, 165, 295	hydrazine, 241, 587
Phoenicin sulphuric acid, 476	propionic acid, 264
Phorone, 169	superoxide, 240
Phosphaniline, 132	Piaselenol, 518
phazobenzene anilide, 80	Piaselenols, 441, 480, 518
chloride, 80	Piazines, 592
Phosphenyl chloride, 132	Piazselenoles, 96
Phosphin, 356, 560	Piazthiolen, 517
Phosphino-benzene, 132	Piazthioles, 96, 441, 479, 480, 518
Phospho-benzene, 132	Picamar, 165
Phosphorphenylamines, 80	Picean ring, 323
Phthalaldehyde, 233	Picene, 416
chlorides, 237	fluorene, 388, 417, 418
dioxime, 233	alcohol, 417, 419
aldehydic acid, 235, 236, 257	ketone, 417, 419
methyl ether, 236	perhydride, 416
amic acid, 240	Picenic acid, 408, 417
anil, 241, 350	l'icoline acrylic acid, 538
azine, 233, 463, <b>586</b>	lactic acid, 538
azines, 586	methyl ketone, 535
azone, 236, 587	Picolines, 532
Phthalein, 364, 586	Picolinic acid, 531, 536
Phthaleins, 351, 363	Picolyl alkines, 535
Phthalic acid, 191	methyl alkine, 535
aldehydes, 233	trichlor methyl alkine, 535
acids, 238, 239	Picramic acid, 154
anhydride, 240, 463	Picramide, 68, 93
diamide, 240	Picrate, 179
•	

Picric acid, 68, 150, 394, 467
Diameterials said 141
Picrocyaminic acid, 151
erythrin, 229
toxic acid, 432
toxin, 432
Picryl chloride, 68
Picylenmethane, 418
Pilocarpidine, 565
coming for
carpine, 565 Pimaric acid, 334
Pimaric acid, 334
Pimelic acid, 314, 522
Dimelin and
Pimelin, 296
ketone, 307
Pimpinella anisum, 269
Pinacoline, 418
Pinene, 25, 308, 322
glycol, 325
hydrobromide, 323
-l-lid- aaa
chloride, 323
nitrosobromide, 323
chloride, 323
Pinic acid, 323
Pinite, 295
Pinol, 325
dibermide 206
dibromide, 326
glycol, 326
hydrate, 325
nitrosochloride, 326
D'
Pinonic acid, 323, 328
Pinoyl formic acid, 323
Pinus lambertina, 295
maritima, 334
Pinylamine, 323, 326
Pipecolines, 540
Pinecolinia acid 540
Pipecolinic acid, 540
Piperazine, 443
Piperazines, 594
Piper betle, 270
1 iper seite, 2/0
cubeba, 272
hydronic acid, 283
Piperic acid, 285, 289
Piperidine, 285, 442, 472
Piperidines, 538
Piperidyl urethane, 540
Pinerine 540 560
riperine, 540, 502
Piperine, 540, 562 Piperonal, 220, 270
acetalamine, 578
Pinemanul carbovalic acid are are
Piperonoyl carboxylic acid, 259, 270
Piperonyl acrolein, 27
acrylic acid, 283
alcohol, 218
Piperonylene acetone, 273
malonic acid, 2. 9
pyroracemic acid, 287
Pineronulio acid 228 270
Piperonylic acid, 228, 270
idene acetone, 273
Piperyl-amido-cyanidine, 605
hydrazine, 540
methyl thiazoline, 507

```
Pipitzaholc acid, 170
Pitch, 49
Pittical, 361
Polei oils, 320
Polybenzoyl cyanide, 258
    carboxylic acids, 238
Polygonin, 431
Polygonum cuspidatum, 431
Polyhaloid phenols, 149
    membered rings, 435
Polymeric aldehyde, 442
          cyanogen compounds, 442
Polymerization, 43, 436
Polymitrohydrocarbons, 66
    oxyanthraquinone, 429
    phenylamines, 79
           fatty hydrocarbons, 335
    quinoyl compounds, 170
    quinoyls, 170
    salicylide, 225
    sulphonic acids, 136
    terpenes, 308
Ponceau dyes, 403
Populin, 430
Populus tremula, 430
Potassium carbon monoxide, 166
           chloranilate, 170
          euthiocarbonate, 170
                 chromate, 164
          indoxyl sulphate, 468
          oxybenzylsulphonate, 184
           phthalimide, 79
Potential valence, 436
Prehnidine, 76
Prehnitic acid, 56, 246
Prehnitol, 56
Prehnitylic acid, 56, 196
Pricrylmalonic ester, 262
Primary amines, 396
Prism formula, 40
Propenyl anisol, 269
          benzene, 268
          benzoic acid, 273
          phenol, 269
          pyrocatechol, 270
          trimethoxybenzene, 270
          veratrol, 270
Propidene-phenylhydrazone, 466, 467
           phthalide, 286
Propionylacetophenone, 250
         benzene, 189
         fenchylamine, 326
         methylphenylhydrazide, 471
         phenol, 221
Propiophenone, 189
Propyl acetanilide, 82
       benzene, 55
benzoic acid, 195
        benzoic ester, 198
```

Propyl chlorphthalazone, 586 Propylene urea, 503 glyoxalidine, 499 mesitylene, 57 phenol, 144 phthalazone, 587 piperidine, 540, 562 pyridene, 532 pyrogallol ether, 165 tetraoxybenzene, 166 Protocatechuic acid, 237, 282 aldehyde, 219 methylene ether, 220 Protocotoln, 349 Pseudoazimide group, 398 azimides, 480, 509 azimide-derivatives, 115 carbostyril ethers, 548 conhydrin, 535, 564 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 159 cunylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 flyoli)-acetic acid, 196 flyoliy-acetic acid, 196 flyo		
Propleme urea, 503 glyoxalidine, 499 mesitylene, 57 phenol, 144 phthalazone, 87 piperidine, 532 pyrogallol ether, 165 tetraoxybenzene, 166 Protocatechuic acid, 227, 282 aldehyde, 219 methylene ether, 220 Protocotofn, 349 Pseudoazimide group, 398 azimide- derivatives, 115 carbostyril ethers, 548 conhydrin, 535, 564 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 145 carboxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 488 sulphonic acid, 485 carboxylic acid, 485 carboxylic acid, 485 carboxylic acid, 485 carboxylic acid, 486 carboxylic acid	Propyl chlorphthalazone, 586	Pyranine, 525 -
glyoxalidine, 499 mesitylene, 57 phenol, 144 phthalazone, 387 piperidine, 540, 562 pyridene, 532 pyrogallol ether, 165 tetraoxybenzene, 166 Protocatechuic acid, 227, 282 aldehyde, 219 methylene ether, 220 Protocotofn, 349 Pseudoazimide group, 398 azimide-derivatives, 115 carbostyril ethers, 548 conhydrin, 535, 564 cumenol, 144 cumenol, 144 cumenol, 144 cumenyl glycol, 232 cumidine, 66 cumoquinone, 169 cumoquinone, 169 cumoquinone, 169 cumoquinone, 169 cumoquinone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Pyralin, 430 Pyrazoles, 149, 487 carboxylic acid, 485 carboxylic acid, 486 carboxylic acid, 485 carboxylic acid, 486 carboxylic acid, 485 carboxylic acid, 486 carboxylic acid, 486 carboxylic a		
mesitylene, 57 phenol, 144 phthalazone, 587 piperidine, 540, 562 pyridene, 532 pyrogallol ether, 165 tetraoxybenzene, 166 Protocatechuic acid, 247, 282 aldehyde, 219 methylene ether, 220 Protocotofn, 349 Pseudoazimide group, 398 azimides, 480, 509 azimide-derivatives, 115 carbostyril ethers, 548 conhydrin, 535, 564 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 144 cumenol, 144 cumenol, 144 cumenol, 144 cumenol, 144 cumenol, 146 cumoquinone, 169 cumylglyoxlic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 Pyralin, 420 Pyrehulis ajoxan, 56, 144 Pulegon, 296 lamide, 428 carboxylic acid, 537 Purpur, French, 162 Purpurin, 420 Rupurp, French, 162 Purpurin, 420, 428 carboxylic acid, 537 Purpur, French, 162 Purpurin, 420, 428 carboxylic acid, 537 Pyridone, 534 Pyridone, 534 Pyridazines, 592 Pyrazole, 124, 437, 479, 480, 481 blue, 488 carboxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 481 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 485 sulphonic acids, 485 sulphonic acids, 485 sulphonic acids, 483 tricarboxylic acid, 485 erroxylic acid, 485 pyrazolione, 480, 481, 490 pyrazolione, 480, 481, 490, 481 pyrazoline, 480, 481, 490 pyrazolione, 480, 481, 490, 481 pyrazoline, 480, 481, 490 pyrazolione, 480, 481, 490, 481 pyrazoline, 480, 481, 490 pyrazolione, 480, 481, 490 pyrazolione, 480, 481, 490 pyrazolione, 480, 481, 490 pyraz		
phenol, 144 phthalazone, 587 piperidine, 540, 562 pyridene, 532 pyrogallol ether, 165 tetraoxybenzene, 166 Protocatechuic acid, 227, 282 aldehyde, 219 methylene ether, 220 Protocotoln, 349 Pseudoazimide group, 398 azimide, 480, 509 azimide, 480, 509 azimide, 545, 564 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 144 cumenol, 144 cumenol, 144 cumenylglycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 238 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 Pryalin, 430 Pyrazolon, 259, 480, 481, 490, 491 Pyrazolon, 480, 481, 490, 491 Pyrazolon, 26, 480, 481, 490, 491 Pyrazolon, 480, 481, 490, 491 Pyrazolon, 480, 481, 490, 491 Pyrazolon, 259, 480, 481, 490, 491 Pyrazolon, 250, 481, 490, 491 Pyrazolon, 260, 481, 490, 491 Pyrazolon, 260, 481,		dicarboxylic seid for
phthalazone, 587 piperidine, 540, 562 pyridene, 532 pyrogaliol ether, 165 tetracaybenzene, 166 Protocatechuic acid, 227, 282 aldehyde, 219 methylene ether, 220 Protocotofn, 349 Pseudoazimide group, 398 azimides, 480, 509 azimide-derivatives, 115 carbostyril ethers, 548 conhydrin, 535, 564 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 144 cumenol, 144 cumenol, 144 cumenol, 144 cumenily glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 Ptyalin, 420 Pyrenyl-acetic acid, 196 Ptyalin, 430 Pyrehotis ajovan, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Pure yellow, 115, 137 Pulejone, 320 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 amide, 488  carboxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 485 silver, 481 sulphonic acids, 485 silver, 481 sulphonic acids, 485 extroxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 485 extroxylic acid, 485 formation, 127 proup, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 485 dicarboxylic acid, 485 formation, 127 proup, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 483 tricarboxylic acid, 485 extroxylic acid, 485 formation, 127 proup, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 486 dicarboxylic acid, 485 extroxylic acid, 485 sulphonic acids, 483 fricarboxylic acid, 485 extroxylic acid, 485 sulphonic acids, 484 extroxyler, 248 sulphonic, 24 pryrazolidine, 480, 481, 490 carboxylic acid, 485 extroxyler, 248 extroxyler g		
piperidine, 540, 562 pyridene, 532 pyrogallol ether, 165 tetraoxybenzene, 166 Protocatechuic acid, 227, 282 aldehyde, 219 methylene ether, 220 Protocotoln, 349 Pseudoszimide group, 398 azimide, 480, 509 azimido-derivatives, 115 carbostyril ethers, 548 conhydrin, 535, 564 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 144 cumenol, 144 cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 486 pletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyslin, 430 Pyrchottis ajoran, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Purpur, French, 162 Purpuri, 420, 428 amide, 428 carboxylic acid, 429  retracarboxylic acid, 537 pridome starboxylic acid, 537 pyridome, 534  tetracarboxylic acid, 485 carboxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 dicarboxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 481 ketones, 484 monazole group, 480 silver, 481 monazole group, 480 silver, 481 ketones, 484 monazole group, 480 silver, 481 carboxylic acid, 485 carboxylic acid, 486 carboxylic acid, 489 carboxylic acid, 480 carboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 48		
pyridene, 532 pyrogallol ether, 165 tetraoxybenzene, 166 Protocatechuic acid, 227, 282 aldehyde, 219 methylene ether, 220 Protocotoln, 349 Pseudoazimide group, 398 azimides, 480, 509 azimido-derivatives, 115 carbostyril ethers, 548 conhydrin, 535, 564 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 144 cumenol, 144 cumenol, 144 cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 28 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Pyrazole, 124, 437, 479, 480, 481 dicarboxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 490 silver, 481 sulphonic acids, 484 monazole group, 480, 481, 490 carboxylic acid, 495 silver, 481 sulphonic acids, 485 carboxylic acid, 485 pyrazoles, 480, 482 pyrazoleine, 480, 481, 490 carboxylic acid, 490 pyrazoloine, 480, 481, 490 carboxylic acid, 486 carboxylic acid, 496 carboxylic acid, 486 carboxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 340 silver, 481 sulphonic acids, 485 carboxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480, 481, 490 carboxylic acid, 485 carboxylic acid, 486 ca		
pyrogallol ether, 165 tetraoxybenzene, 166 Protocatechuic acid, 227, 282		
tetraoxybenzene, 166 Protocatechuic acid, 227, 282 aldehyde, 219 methylene ether, 220 Protocotoln, 349 Pseudoazimide group, 398 azimides, 480, 509 azimides, 480, 509 azimides, 480, 509 azimide, 49, 53, 554 cumene, 49, 53, 554 cumene, 49, 53, 554 cumene, 144 cumenol, 144 cumenol, 144 cumenol, 144 cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoln, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 P/Yecketis ajovean, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Pulvic acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 amide, 428 carboxylic acid, 485 dicarboxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 485 sulphonic acids, 485 sulphonic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 485 carboxylic acid, 485 carboxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 485 carboxylic acid, 486 carboxylic acid, 485 carboxylic acid, 485 carboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 486 carboxy		Pyrazines, 592
tetraoxybenzene, 166 Protocatechuic acid, 227, 282 aldehyde, 219 methylene ether, 220 Protocotoln, 349 Pseudoazimide group, 398 azimides, 480, 509 azimides, 480, 509 azimides, 480, 509 azimide, 49, 53, 554 cumene, 49, 53, 554 cumene, 49, 53, 554 cumene, 144 cumenol, 144 cumenol, 144 cumenol, 144 cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoln, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 P/Yecketis ajovean, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Pulvic acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 amide, 428 carboxylic acid, 485 dicarboxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 485 sulphonic acids, 485 sulphonic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 485 carboxylic acid, 485 carboxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 485 carboxylic acid, 486 carboxylic acid, 485 carboxylic acid, 485 carboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 486 carboxy	pyrogallol ether, 165	Pyrazole, 124, 437, 479, 480, 481
methylene ether, 220 Protocotoln, 349 Pseudoazimide group, 398 azimides, 480, 509 azimido-derivatives, 115 carbostyril ethers, 548 conhydrin, 535, 564 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 146 cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydhantoic acid, 88 hydantoln, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Prichetis ajorean, 56, 144 Pyridazinone-carboxylic acid, 585 group, 439, 442 Pyridazinone-carboxylic acid, 489 opyrazolon, 489 Pyrene, 48, 481, 490 carboxylic acids, 490 Pyrazolidie, 480 dicarboxylic acid, 485 formation, 127 group, 489, 481 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 485 carboxylic acid, 485 carboxylic acids, 485 carboxylic acids, 486 dicarboxylic acids, 486 carboxylic acids, 486 carboxylic acid, 489 opyrazolon, 489 Pyrene, 48, 481 sulphonic acids, 483 dicarboxylic acid, 485 carboxylic acid, 485 carboxylic acid, 485 carboxylic acid, 485 carboxylic acid, 486 carboxylic acid, 489 opyrazolon, 489, 481, 486 carboxylic acid,	tetraoxybenzene, 166	blue, 488
methylene ether, 220 Protocotoln, 349 Pseudoazimide group, 398 azimides, 480, 509 azimido-derivatives, 115 carbostyril ethers, 548 conhydrin, 535, 564 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 146 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoln, 88 phthalimidine, 233 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Prichetis ajoran, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Pulvia acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 429  Pyridone, 534  carboxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acid, 485 carboxylic acid, 485 ester, 484 Pyrazolidine, 480, 481, 490 carboxylic acid, 485 carboxylic acid, 486 dicarboxylic acids, 490 Pyrazoline, 480, 481, 490 carboxylic acid, 486 dicarboxylic acid, 486 dicarboxylic acid, 486 ester, 484 Pyrazoles, 480 dicarboxylic acid, 485 carboxylic acid, 486 poprazoline, 480, 481, 490 carboxylic acid, 480 carboxylic acid, 486 carboxylic acid, 485 carboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 486 carboxylic acid,	Protocatechuic acid, 227, 282	carboxylic acid, 485
Protocotoln, 349 Pseudoazimide group, 398     azimides, 480, 509     azimide-derivatives, 115     carbostyril ethers, 548     conhydrin, 535, 564     cumene, 49, 53, 55     sulphonic acid, 144     cumenyl glycol, 232     cumidine, 76     cumoquinone, 169     cumylglyoxylic acid, 259         hydrazine, 120     indoxyl, 469     ionone, 310     isatin ethoxime, 472     isatoxime, 469, 472     leucaniline, 352     lutidostyril, 534         carboxylic acid, 538     morphine, 576     nitroso-anthrone, 423     opianic acid, 238     pelletierine, 571     phenanthrolines, 554     phenyl-acetic acid, 196     thiohydantoic acid, 88     hydantoin, 88     phthalimidine, 234     purpurin, 429     saccharin-chloride, 216     tolyl-acetic acid, 196 Plyalin, 430  //tychetis ajovan, 56, 144 Pulegon, 296     amine, 317 Pulejone, 320 Pulvic acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428     -amide, 428     carboxylic acid, 429  monazole group, 439, 441 ketones, 484     monazole group, 480     silver, 481     sulphonic acids, 483     tricarboxylic acid, 485     sulphonic acids, 483     tricarboxylic acid, 486     carboxylic acid, 486     ester, 484  Pyrazoles, 480, 481, 490     carboxylic acid, 486     pyrazolione, 480, 481, 490     carboxylic acid, 486     carboxylic acid, 537     pyridzine, 50, 481, 482     pyrazolione, 480, 481, 490     carboxylic acid, 486     carboxylic acid, 486     carboxylic acid, 486     carboxylic acid, 485     carboxylic acid, 486     carbox		acids, 484
Protocotoln, 349 Pseudozzimide group, 398 azimides, 480, 509 azimido-derivatives, 115 carbostyril ethers, 548 conhydrin, 535, 564 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 146 cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 486 dicarboxylic acids, 490 Pyrazolidone, 480, 481, 490, 481 Pyrazolidone, 480, 481, 485 carboxylic acids, 490 Pyrazolidone, 480, 481, 490, 481 Pyrazolidone, 480, 481, 486 dicarboxylic acids, 486 dicarboxylic acids, 486 dicarboxylic acids, 486 dicarboxylic acid, 486 ester, 486 tricarbonacetic trimethyl este 486 Pyrazolon, 259, 480, 481, 486, 487 azobenzene, 487 carboxylic acid, 489 opprazolon, 489 Pyrazolidone, 480, 481, 480 dicarboxylic acids, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 483 tricarboxylic acids, 485 carboxylic acids, 486 dicarboxylic acids, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 485 carboxylic acid, 485 carboxylic acid, 485 formation, 127 group, 439, 441 ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 485 carboxylic acid, 485 carboxylic acids, 486 dicarboxylic acids, 486 dicarboxylic acids, 486 carboxylic acids, 486 fricarboxylic acids, 486 fricarboxylic acids, 486 fricarboxylic acid, 486 carboxylic acid, 486 pyrazolidone, 480, 481, 490 carboxylic acid, 538 dicarboxylic acid, 486 dicarboxylic acid, 486 carboxylic acid, 486 pyrazolione, 480, 481, 486 carboxylic acid, 538 pydan, 411 ketones, 484 monorazole group, 4		
Protocotoln, 349 Pseudoazimide group, 398    azimides, 480, 509    azimides, 480, 505    sulphonic acid, 144    cumenel, 144    cumenel, 144    cumenel, 144    cumenyl glycol, 232    cumidine, 76    cumoquinone, 169    cumylglyoxylic acid, 259         hydrazine, 120    indoxyl, 469    ionone, 310    isatin ethoxime, 472    isatoxime, 469, 472    leucaniline, 352    lutidostyril, 534         carboxylic acid, 538    morphine, 576    nitroso-anthrone, 423    opianic acid, 238    pelletierine, 571    phenanthrolines, 554    phenyl-acetic acid, 196    thiohydantoic acid, 88    hydantoin, 88    phthalimidine, 231    purpurin, 429    saccharin-chloride, 216    tolyl-acetic acid, 196    Pyraldin, 430    Pyraldin, 430		
Pseudoazimide group, 398 azimides, 480, 509 azimide-derivatives, 5115 carbostyril ethers, 548 conhyl, 635, 554 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 144 cumenol, 144 cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Pytalin, 430 Pyta		
azimides, 480, 509 azimido-derivatives, 115 carbostyril ethers, 548 conhydrin, 535, 564 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 144 cumenol, 144 cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxine, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic, 88 hydantofn, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 (**Ytchotis ajoxan, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Pulvic acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 arrboxylic acid, 429  **Ketones, 484 monazole group, 480 silver, 481 sulphonic acids, 485 sulphonic acids, 485 carboxylic acids, 490 Pyrazolidne, 480, 481, 490 carboxylic acids, 496 carboxylic acids, 486 dicarboxylic acids, 486 dicarboxylic acid, 486 ester, 486 firicarbonylic acids, 490 Pyrazolidne, 480, 481, 490 carboxylic acids, 486 dicarboxylic acids, 486 dicarboxylic acid, 486 ester, 484 monazole group, 480 silver, 481 sulphonic acids, 485 sulphonic acids, 485 carboxylic acids, 490 Pyrazolidne, 480, 481, 490 carboxylic acid, 486 dicarboxylic acid, 486 ester, 486 dicarboxylic acid, 486 ester, 486 firicarbonylic acid, 486 dicarboxylic acid, 486 ester, 486 dicarboxylic acid, 486 ester, 484  Pyrazolidne, 480, 481, 490 carboxylic acid, 486 dicarboxylic acid, 486 ester, 486 Pyrazolidne, 480, 481, 490 carboxylic acid, 486 dicarboxylic acid, 486 ester, 486 firicarbonylic acid, 487 exproacidine, 480, 481, 490 carboxylic acid, 486 ester, 486 firicarbonylic acid,		, , , , , , , , , , , , , , , , , , ,
azimido-derivatives, 115 carbostyril ethers, 548 conhydrin, 535, 564 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 144 cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Pyridazinone-carboxylic acid, 585 Pyridazinone-carboxylic acid, 536 group, 439, 442 Pyridazinone-carboxylic acid, 585 Pyridazinone-carboxylic acid, 536 group, 439, 442 Pyridazinone-carboxylic acid, 537 polycarboxylic acid, 537 polycarboxylic acid, 537 polycarboxylic acid, 537 rticarboxylic acid, 537 Pyridone, 534  rticarboxylic acid, 485 sulphonic acids, 483 tricarboxylic acids, 483 tricarboxylic acids, 485 carboxylic acid, 486 carboxylic acid, 490 Pyrazolidne, 480, 481, 490, 491 Pyrazolione, 480, 481, 490, 491 Pyrazolione, 480, 481, 490, 481 Pyrazolione, 480, 481, 490 carboxylic acid, 486 Pyrazolone, 480, 481, 490 carboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 480 Pyrazolione, 480, 481, 490, 491 Pyrazoline, 480, 481, 490, 481 Pyrazoline, 480, 481, 490 Pyrazoline, 480, 481, 490 Carboxylic acid, 486 carboxylic acid, 480 carboxylic acid, 480 pyrazolone, 480 Pyrazolone, 480 carboxylic acid, 480 carboxylic acid, 480 carboxylic acid, 48		
silver, 481 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 144 cumenol, 144 cumenol, 169 cumoquinone, 169 cumoquinone, 169 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoln, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptytalin, 430  //techetis ajoxean, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 429  syrazoles, 480, 481, 490, 491 Pyrazolide, 480, 481, 490, 491 Pyrazoline, 480, 481, 490 carboxylic acid, 486 carboxylic acid, 486 carboxylic methyl este 486 Pyrazolon, 259, 480, 481, 490, 491 Pyrazolone, 480, 481, 490, 491 Pyrazoline, 480, 481, 490, 491 Pyrazoline, 480, 481, 490, 491 Pyrazolone, 480, 481, 490, 491 Pyrazoline, 480 carboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 486 Pyrazolon, 259, 480 carboxylic acid, 486 poptracine, 570 prene, 320 Pyrene, 48, 452 Pyrazolone, 480 carboxylic acid, 486 carboxylic acid, 486 poptracine, 490 pyrazolone, 480, 481, 490, 491 Pyrazoline, 480 carboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 486 poptracine, 490 pyrazolone, 490, 481, 486 carboxylic acid, 538 dicarboxylic acid, 535 group, 442, 526 pentacarboxylic acid, 537 polycarboxy		
sulphonic acids, 483 cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 144 cumenol, 144 cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 //trchotis ajoxean, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Pulvic acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 429  sulphonic acids, 483 tricarboxylic acids, 490 Pyrazolidone, 480, 481, 490, 491 Pyrazolidne, 480, 481, 490 carboxylic acid, 486 carboxylic acid, 489 opyrazolon, 259, 480, 481, 490, 491 Pyrazolidne, 480, 481, 490 Pyrazolidne, 480, 481, 490, 491 Pyrazolidne, 480, 481, 490 carboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 489 opyrazolon, 259, 480, 481, 490, 491 Pyrazolidne, 480, 481, 490 carboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 489 opyrazolon, 259, 480, 481, 490, 491 Pyrazolidne, 480, 481, 490 Pyrazolidne, 480, 481, 490 Pyrazolidne, 480, 481, 490 Pyrazolidne, 480, 481, 490 Pyrazolidne, 480, 481 Pyrazolidne, 480, 481 carboxylic acid, 486 carboxylic acid, 480 opyrazolon, 259 ketone, 420 Pyridazine, 54, 486 carboxylic acid, 489 opyraz		
cumene, 49, 53, 55 sulphonic acid, 144 cumenol, 144 cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin cthoxime, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoln, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Pyrazoles, 480, 481, 490 carboxylic acids, 490 Pyrazolidine, 480, 481, 485, 486 carboxylic acid, 486 dicarboxylic acid, 486 dicarboxylic acid, 486 ester, 484 Pyrazoles, 480, 481, 490, 491 Pyrazolidine, 480, 481, 485, 486 carboxylic acid, 486 dicarboxylic acid, 486 dicarboxylic acid, 486 ester, 484 Pyrazoles, 480, 482 Pyrazoles, 480, 482, 490, 491 Pyrazoline, 480, 481, 495, 486 dicarboxylic acid, 486 dicarboxylic acid, 486 ester, 484 Pyrazoles, 480, 482, 490, 491 Pyrazolidine, 480, 481, 490, 491 Pyrazoline, 480, 481, 490, 491 Pyrazolidine, 480, 481, 490, 491 Pyrazolidene, 480, 481, 495, 490 carboxylic acids, 486 dicarboxylic acid, 486 ester, 484 Pyrazoles, 480, 481, 485, 486 carboxylic acids, 486 dicarboxylic acid, 486 ester, 484 Pyrazolidene, 480, 481, 485, 486 dicarboxylic acid, 486 ester, 484 Pyrazolidene, 480, 481, 490, 491 Pyrazolidene, 480, 481, 490, 491 Pyrazolidene, 480, 481, 485, 486 carboxylic acids, 486 dicarboxylic acids, 486 Pyrazolon, 259, 480, 481, 486 earboxylic acid, 486 earboxylic acid, 486 earboxylic acid, 486 Pyrazolon, 259, 480, 481, 486 earboxylic acid, 489 opyrazolon, 489 Pyrene, 48, 420, 576 ketone, 420 Pyrene, 48, 420, 556 dicarboxylic acid, 585 group, 439, 442 Pyridazine, 584, 585 dicarboxylic acid, 585 group, 439, 442, 526 poptracidane, 480 dica		
sulphonic acid, 144 cumenol, 144 cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Ptychotis ajorwan, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Pulvic acid, 382 Purpuylic acid, 429 Pyrazolidine, 480, 481, 490 carboxylic acids, 486 dicarboxylic acids, 486 carboxylic acids, 486 carboxylic acids, 486 carboxylic acid, 486 Pyrazolidine, 480, 481, 490 carboxylic acids, 486 dicarboxylic acids, 486 carboxylic acids, 486 carboxylic acid, 587 pyrazolon, 259, 480, 481, 490, 481 Pyrazolidne, 480, 481 Pyrazolidne, 480, 481 Pyrazolidne, 480, 481 Carboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 486 carboxyli	conhydrin, 535, 564	sulphonic acids, 483
sulphonic acid, 144 cumenol, 144 cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoln, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Ptychotis ajorean, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Pulvic acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 429 Pyrazolidine, 480, 481, 490 carboxylic acids, 486 dicarboxylic acid, 486 carboxylic acid, 486 extroxylic acids, 486 dicarboxylic acid, 486 carboxylic acid, 486 Pyrazoloine, 480, 481, 490 carboxylic acids, 486 dicarboxylic acids, 486 dicarboxylic acids, 486 dicarboxylic acids, 486 carboxylic acid, 486 Pyrazoloine, 480, 481, 490 carboxylic acids, 486 dicarboxylic acids, 486 dicarboxylic acid, 486 carboxylic acid, 486 Pyrazoloine, 480, 481, 490 carboxylic acids, 486 dicarboxylic acids, 486 carboxylic acid, 486 carboxylic acid, 486 Pyrazoloine, 480, 481, 490 carboxylic acids, 486 dicarboxylic acid, 486 carboxylic acid, 486 Pyrazolidine, 480, 481, 490 carboxylic acids, 486 dicarboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 486 Pyrazolione, 480, 481, 490 carboxylic acids, 486 carboxylic acid, 486 carboxylic acid, 486 Pyrazolione, 480, 481, 490 carboxylic acids, 486 dicarboxylic acid, 587 proprazolon, 489 Pyrene, 48, 420, 576 ketone, 420 Pyrenic acid, 4	cumene, 49, 53, 55	tricarboxylic acid, 485
cumenol, 144 cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Pyrazoloidine, 480, 481, 490 Pyrazolidine, 480, 481, 485, 486 carboxylic acids, 486 carboxylic acids, 486 carboxylic acid, 486 carboxylic methyl este 486 Pyrazolon, 259, 480, 481, 485, 486 carboxylic acid, 489 opyrazolon, 29, 480, 481, 485, 486 carboxylic acid, 486 carboxylic acid, 489 opyrazolon, 296 ketone, 420 Pyridazine, 584, 585 dicarboxylic acid, 585 group, 432, 442, 526 pentacarboxylic acid, 537 polycarboxylic acid, 537 polycarboxylic acid, 537 polycarboxylic acid, 537 tricarboxylic acid, 537 polycarboxylic acid, 537 polycarboxylic acid, 537 polycarboxylic acid, 537 polycar		ester, 484
cumenyl glycol, 232 cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin cthoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Ptyrehotis apirocan, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Pulvic acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 429 Pyrazolidine, 480, 481, 490 carboxylic acids, 486 dicarboxylic acids, 486 tricarbonacetic trimethyl este 486 Pyrazolon, 259, 480, 481, 486, 487 azobenzene, 489 carboxylic acid, 486 exarboxylic acid, 486 pyrazolone, 480, 481, 490, 491 Pyrazoline, 480, 481, 490, 491 Pyrazoline, 480, 481, 490, 491 Pyrazoline, 480, 481, 495 carboxylic acid, 586 carboxylic acid, 486 extricarboxylic acid, 486 exarboxylic acid, 486 exarboxylic acid, 486 pyrazolone, 480, 481, 495, 486 carboxylic acids, 486 dicarboxylic acid, 486 exploy ylic acid, 486 exploy ylic acids, 489 exploy ylic acids, 489 exploy ylic acids, 489 exp		
cumidine, 76 cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxine, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Pyrazoline, 480, 481, 485, 486 carboxylic acid, 486 carboxylic acid, 486 carboxylic methyl este 486 carboxylic acid, 489 opyrazolon, 259, 480, 481, 486, 487 azobenzene, 486 Pyrazolone, 259, 480, 481, 486, 487 azobenzetic trimethyl este 486 carboxylic acid, 489 opyrazolon, 259, 480, 481, 485, 486 dicarboxylic acid, 486 carboxylic acid, 489 opyrazolone, 480, 481, 485, 486 dicarboxylic acid, 486 carboxylic acid, 489 opyrazolone, 296 ketone, 420 Pyrenci acid, 420 Pyrenci acid, 420 Pyridazine, 584, 585 dicarboxylic acid, 585 group, 439, 442 Pyridazine, 486 carboxylic acid, 489 opyrazolone, 480, 481, 485, 486 dicarboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 489 opyrazolone, 480, 481, 485, 486 dicarboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 489 opyrazolone, 480 carboxylic acid, 486 carboxylic acid, 486 carboxylic acid, 489 opyrazolone, 480 carboxylic acid, 486 carboxylic acid, 489 opyrazolone, 480 carboxylic acid, 486 carboxylic acid, 489 opyrazolone, 480 carboxylic acid, 486 carboxylic acid, 489 opyrazolon, 489 Pyriazoline, 480 carboxylic acid, 489 opyrazolon, 489 Pyrazolone, 480 carboxylic acid, 489 opyrazolon, 489 Pyrene, 48, 420, 576 ketone, 420 Pyridazine, 584, 585 dicarboxylic acid, 585 group, 439, 442 Pyridazinone-carboxylic acid, 537 polyrachotis ajoxen, 56, 144 Pyridazinone-carboxylic acid, 537 polyrachotis ajoxen, 56, 144 Pyridazinone-carboxylic a		
cumoquinone, 169 cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoln, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Pyrazolione, 480, 481, 485, 486 carboxylic acid, 486 carboxylic acid, 486 carboxylic methyl este 486 Pyrazolon, 259, 480, 481, 486, 487 azobenzene, 487 carboxylic acid, 489 opyrazolon, 489 Pyrene, 48, 420, 576 ketone, 420 Pyrenic acid, 420 Pyridazine, 584, 585 dicarboxylic acid, 585 group, 439, 442 Pyridazinone-carboxylic acid, 585 group, 439, 442 Pyridazinone-carboxylic acid, 536 group, 442, 526 pentacarboxylic acid, 537 polycarboxylic acid, 537 tricarboxylic acid, 537 pricarboxylic acid, 537 pridone, 534		
cumylglyoxylic acid, 259 hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 leucaniline, 352 lutidostyril, 534		
hydrazine, 120 indoxyl, 469 ionone, 310 isatin ethoxime, 472 leucaniline, 352 lutidostyril, 534		
indoxyl, 469 ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534 carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Pyralin, 430 //tychotis ajavan, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Purve yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 -amide, 428 carboxylic acid, 486 carboxylic methyl este 486 carboxylic acid, 489 opyrazolon, 259, 480, 481, 486, 487 azobenzene, 487 carboxylic acid, 489 opyrazolon, 489 Pyrene, 48, 420, 576 ketone, 420 Pyrenic acid, 420 Pyrenic acid, 420 Pyrenic acid, 420 Pyridazinone-carboxylic acid, 585 group, 442 Pyridazinone-carboxylic acid, 537 polycarboxylic acid, 536 group, 442, 526 pentacarboxylic acid, 537 polycarboxylic acid, 537 rticarboxylic acid, 537 Pyridone, 534		
ionone, 310 isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534  carboxylic acid, 538 morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Ptyalin, 430 Ptylegon, 296 amine, 317 Pulejone, 320 Purpur, French, 162 Purpurr, French, 162 Purpurin, 428 -amide, 428 carboxylic acid, 429  ester, 486 tricarbonacetic trimethyl este 486 Pyrazolon, 259, 480, 481, 486, 487 azobenzene, 487 carboxylic acid, 429 Pyrene, 48, 420, 576 ketone, 420 Pyrenquinone, 420 Pyridazinone-carboxylic acid, 585 group, 439, 442 Pyridazinone-carboxylic acid, 585 Pyridine, 106, 437, 438, 443, 531 betaine, 446 betaines, 530, 532 carboxylic acid, 537 polycarboxylic acid, 537 polycarboxylic acid, 537 rticarboxylic methyl este 486 Pyrazolon, 259, 480, 481, 486, 487 azobenzene, 487 carboxylic acid, 489 opyrazolon, 489 Pyrene, 48, 420, 576 ketone, 420 Pyrenquinone, 420 Pyridazine, 584, 585 group, 439, 442 Pyridazinone-carboxylic acid, 585 group, 439, 442 Pyridazine, 584 proprincing acid, 489 opyrazolon, 489 Pyrazolon, 259, 480, 481, 486, 487 azobenzene, 487 carboxylic acid, 489 opyrazolon, 489 Pyrene, 48, 420, 576 ketone, 420 Pyridazine, 584 prividazine, 584 group, 439, 442 Pyridazine, 584 group, 430, 442 Pyridazine, 584 group, 439, 442 Pyridazine, 584 group, 430, 442 Pyridazine, 584 group, 439, 442 Pyridazine, 584 group, 430, 442 Pyridazine, 584, 585 group, 439, 442 Pyridazine, 584, 585 group, 439, 442 Pyridazine, 584, 585 group, 430, 442 Pyridazine, 584, 585 group, 430, 442 Pyridazine, 584, 585 group, 430, 442 P		
isatin ethoxime, 472 isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534		
isatoxime, 469, 472 leucaniline, 352 lutidostyril, 534		
leucaniline, 352 lutidostyril, 534  carboxylic acid, 538  morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Ptychotis ajovan, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Purve yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 538  carboxylic acid, 538  Pyrazolon, 259, 480, 481, 486, 487 azobenzene, 487 carboxylic acid, 489 opyrazolon, 489  Pyrene, 48, 420, 576 ketone, 420 Pyrenquinone, 420 Pyrenquinone, 420 Pyridazine, 584, 585 dicarboxylic acid, 585 group, 439, 442 Pyridazinone-carboxylic acid, 585 Pyridine, 106, 437, 438, 443, 531 betaIne, 446 betaInes, 530, 532 carboxylic acid, 536 group, 442, 526 pentacarboxylic acid, 537 polycarboxylic acid, 537 ricarboxylic acid, 537 ricarboxylic acid, 537 Pyridone, 534		
lutidostyril, 534	isatoxime, 469, 472	
morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Ptylalin, 430 Ptylegon, 296 amine, 317 Pulejone, 320 Purpur, French, 162 Purpurin, 428 -amide, 428 carboxylic acid, 429 Pyridazinone-carboxylic acid, 537 Pyridazinone-carboxylic acid, 537 polycarboxylic acid, 537 polycarboxylic acid, 537 Pyridone, 534 Pyridone, 534 Pyridone, 554 Pyridazinone-carboxylic acid, 535 group, 443, 531 betaine, 446 betaines, 530, 532 carboxylic acid, 537 polycarboxylic acid, 537 Pyridone, 534 Pyridone, 534	leucaniline, 352	carboxylic methyl este
morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196	lutidostyril, 534	486
morphine, 576 nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196	carboxylic acid, 538	Pyrazolon, 259, 480, 481, 486, 487
nitroso-anthrone, 423 opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196		azobenzene, 487
opianic acid, 238 pelletierine, 571 phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Pyrenic acid, 420 Pyridazine, 584, 585 dicarboxylic acid, 585 Pyridazine, 584, 585 dicarboxyli		
Pyrene, 48, 420, 576 ketone, 420 Pyrenic acid, 420 Pyrenc, 584, 585 dicarboxylic acid, 585 group, 442, 526 pentacreacid, 537 polycarboxylic acid,		
phenanthrolines, 554 phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Ptychetis ajowan, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Pulvic acid, 382 Pur yellow, 115, 137 Purpur, French, 162 Purpurin, 428 -amide, 428 carboxylic acid, 429  ketone, 420 Pyridazinone-carboxylic acid, 585 group, 439, 442 Pyridazinone-carboxylic acid, 585 Pyridine, 106, 437, 438, 443, 531 betaine, 446 betaines, 530, 532 carboxylic acid, 537 polycarboxylic acid, 537 polycarboxylic acids, 545 sulphonic acids, 537 Pyridone, 534		
phenyl-acetic acid, 196 thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Pyridazinone-carboxylic acid, 585 group, 439, 442 Pyridazinone-carboxylic ester, 585 Pyridine, 106, 437, 438, 443, 531 Pyridine, 46  betaines, 530, 532 carboxylic acid, 536 group, 442 Pyridazinone-carboxylic acid, 537 potatione, 426 petalenes, 530, 532 carboxylic acid, 537 polycarboxylic acid, 537 polycarboxylic acid, 537 polycarboxylic acid, 537 ricarboxylic acid, 537 Pyridone, 534	phenanthrolines, 554	
thiohydantoic acid, 88 hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Pyridazine, 584, 585 group, 439, 442 Pyridazine-carboxylic acid, 585 group, 439, 442 Pyridazinone-carboxylic ester, 585 Pyridine, 106, 437, 438, 443, 531 betaine, 446 betaines, 530, 532 carboxylic acid, 537 Pulejone, 320 Pulvic acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420 Pyridazine, 584, 585 group, 439, 442 betaine, 446 betaines, 530, 532 carboxylic acid, 537 group, 442, 526 pentacarboxylic acid, 537 polycarboxylic acids, 545 sulphonic acids, 533 tetracarboxylic acid, 537 Pyridone, 534	phenyl-acetic acid tob	
hydantoin, 88 phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Pyridazine, 584, 585 dicarboxylic acid, 585 group, 439, 442 Pyridazinone-carboxylic acid, 585 Pyridine, 106, 437, 438, 443, 531 betaine, 446 betaines, 530, 532 carboxylic acid, 537 pulejone, 320 Pulvic acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 -amide, 428 carboxylic acid, 429 Pyridazine, 584, 585 dicarboxylic acid, 585 Pyridazine, 584, 585 dicarboxylic acid, 537 Pyridazine, 584, 585 dicarboxylic acid, 537 Pyridazine, 584, 585 dicarboxylic acid, 585 Pyridazine, 584,		
phthalimidine, 234 purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Ptychotis ajorean, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Pulvic acid, 382 Pure yellow, 115, 137 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 429  dicarboxylic acid, 585 group, 439, 442 Pyridazinone-carboxylic ester, 585 Pyridazinone-carboxylic ester, 585 Pyridazinone-carboxylic acid, 531 Pyridazinone-carboxylic acid, 532 Pyridazinone-carboxylic acid, 531 Pyridazinone-carboxylic acid, 535 Pyridazinone-carboxylic acid, 537 Pyridazinone-carboxylic acid, 537 Pyridazinone-carboxylic acid, 537 Pyridazinone-carboxylic acid, 535 Pyridazinone-carboxylic acid, 537 Pyridazinone-		
purpurin, 429 saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Pyridazinone-carboxylic ester, 585 Pyridine, 106, 437, 438, 443, 531 Pyridazinone-carboxylic ester, 585 Pyridine, 106, 437, 438, 443, 531 Pyridine, 530, 532 carboxylic acid, 531, 535 dicarboxylic acid, 536 group, 442, 526 pentacarboxylic acid, 537 polycarboxylic acid, 537 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 -amide, 428 carboxylic acid, 429 Pyridazinone-carboxylic ester, 585 Pyridine, 106, 437, 438, 443, 531 Pyridine, 106, 437, 438, 443, 531 Pyridine, 106, 437, 438, 443, 531 Pyridine, 530, 532 carboxylic acid, 537 polycarboxylic acid, 537 Pyridone, 534		
Saccharin-chloride, 216 tolyl-acetic acid, 196 Ptyalin, 430 Ptychotis ajorean, 56, 144 Pulegon, 296 amine, 317 Pulejone, 320 Pulvic acid, 382 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 429 Pyridazinone-carboxylic ester, 585 Pyridine, 106, 437, 438, 443, 531 betaIne, 446 betaInes, 530, 532 carboxylic acid, 536 group, 442, 526 pentacarboxylic acid, 537 polycarboxylic acids, 545 sulphonic acids, 533 tetracarboxylic acid, 537 Pyridone, 534		
tolyl-acetic acid, 196 Ptyalin, 430 Ptychefts ajorean, 56, 144 Pulegon, 296     amine, 317 Pulejone, 320 Pulvic acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428     -amide, 428     carboxylic acid, 429 Pyridine, 106, 437, 438, 443, 531 betaIne, 446 betaInes, 530, 532 carboxylic acid, 537, 535 dicarboxylic acid, 536 group, 442, 526 pentacarboxylic acid, 537 polycarboxylic acids, 545 sulphonic acids, 533 tetracarboxylic acid, 537 Pyridone, 534		
Ptyalin, 430  Ptychotis ajowan, 56, 144  Pulegon, 296 amine, 317  Pulejone, 320 Pulvic acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 429  Pyridone, 534  betaIne, 446 betaInes, 530, 532 carboxylic acid, 531, 535 dicarboxylic acid, 536 group, 442, 526 pentacarboxylic acid, 537 polycarboxylic acids, 545 sulphonic acids, 533 tetracarboxylic acid, 537 Pyridone, 534		
Pulegon, 296 amine, 317 Pulejone, 320 Pulvic acid, 382 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 429 Pyridone, 534 Pyridone, 537 Pyridone, 534  betaînes, 530, 532 carboxylic acid, 531, 535 dicarboxylic acid, 536 group, 442, 526 pentacarboxylic acid, 537 polycarboxylic acids, 545 sulphonic acids, 533 tetracarboxylic acid, 537 Pyridone, 534		
Pulegon, 296 amine, 317  Pulejone, 320 Pulvic acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 429  Pyridone, 534  carboxylic acid, 531, 535 dicarboxylic acid, 536 group, 442, 526 pentacarboxylic acid, 537 polycarboxylic acid, 545 sulphonic acids, 533 tetracarboxylic acid, 537 Pyridone, 534		
nmine, 317  Pulejone, 320  Pulvic acid, 382  Pure yellow, 115, 137  Purpur, French, 162  Purpurin, 420, 428  -amide, 428  carboxylic acid, 429  Pyridone, 534  dicarboxylic acid, 536  group, 442, 526  pentacarboxylic acid, 537  polycarboxylic acid, 545  sulphonic acids, 533  tetracarboxylic acid, 537  Pyridone, 534	Ptychotis ajowan, 56, 144	betaines, 530, 532
nmine, 317  Pulejone, 320  Pulvic acid, 382  Pure yellow, 115, 137  Purpur, French, 162  Purpurin, 420, 428  -amide, 428  carboxylic acid, 429  Pyridone, 534  dicarboxylic acid, 536  group, 442, 526  pentacarboxylic acid, 537  polycarboxylic acid, 545  sulphonic acids, 533  tetracarboxylic acid, 537  Pyridone, 534	Pulegon, 296	carboxylic acid, 531, 535
Pulejone, 320 Pulvic acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 429  group, 442, 526 pentacarboxylic acid, 537 polycarboxylic acid, 537 sulphonic acida, 533 tetracarboxylic acid, 537 tricarboxylic acid, 537 Pyridone, 534	amine, 317	dicarboxylic acid, 536
Pulvic acid, 382 Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 429  Pyridone, 534  pentacarboxylic acid, 537 polycarboxylic acid, 545 sulphonic acids, 533 tetracarboxylic acid, 537 ricarboxylic acid, 537 Pyridone, 534		
Pure yellow, 115, 137 Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 429  Pyridone, 534  polycarboxylic acids, 545 sulphonic acids, 533 tetracarboxylic acid, 537 tricarboxylic acid, 537 Pyridone, 534	Pulvic acid, 382	
Purpur, French, 162 Purpurin, 420, 428 -amide, 428 carboxylic acid, 429  Sulphonic acida, 533 tetracarboxylic acid, 537 tricarboxylic acid, 537 Pyridone, 534		
Purpurin, 420, 428 -amide, 428 carboxylic acid, 429  tetracarboxylic acid, 537 tricarboxylic acid, 537 Pyridone, 534		
-amide, 428 tricarboxylic acid, 537 carboxylic acid, 429 Pyridone, 534		
carboxylic acid, 429 Pyridone, 534		
Purpuroxanthin, 428 Pyridones, 522		
a urpurovantum, 420 r fridones, 522		Puridones 133
	- wpulokalitilii, 420	- 1

Pyridyl acrylic acid, 538	Pyrrol, 437, 438, 441, 443, 447, 457, 462,
alcohols, 535	
	465, 479, 480
alkines, 535	azo benzene, 460
brompropionic acid, 538	carbamide, 458
ethyl alkine, 535	carboxylic acids, 460, 461
ketone, 535	ester, 458
ketones, 535	diazo benzene, 460
lactic acid, 538	dicarboxylic acid, 461
methyl ketone, 535	Pyrrolen-phthalide, 461
pyrrolidine, 462	glyoxylic acid, 460
pyrrol, 458, 459	Pyrrolidine, 461, 480
tetrahydro-methyl pyrrol, 565	l'yrrolidone, 462, 480
	Durroline 46. 480
Pyrimidine group, 439, 442	Pyrroline, 461, 480
Pyrimidines, 587	Pyrrolon, 480
Pyrocatechin, 159	Pyrrol red, 457
carbonic ester, 159	Pyrrolylene, 462
carboxylic acid, 228	Pyrro-monazole, 480, 496
chlorphosphine, 159, 160	group, 480
diacetyl ester, 159	monazoles, 479
benzoyl ester, 159	triazole, 480, 519
methyl ether, 159	triazoles, 479, 519
ethylene ester, 159	Pyrroyl-pyrrol, 460
monobenzoyl ester, 159	Pyrryl-dimethyl diketone, 460
methyl ether, 159	methyl ketone, 460
oxychlorphosphine, 159, 160	
sulphite, 159	
catechol, 159	0
cylic esters, 160	Q.
hetero-ring formations from,	QUATERNARY ammonium derivatives, 73
159	Quebrachite, 295
homologues, 160	Quebracho-bark, 295
sulphuric acid, 159	Quercetin, 523
Pyrocoll, 460, 461, 468	Quercite, 295
comane, 522	Quercitrin, 432
comenic acid, 522	Quercus tinctoria, 432
condensation, 43	Quina-bases, 571
gallol, 164, 464	acetophenone, 221
carboxylic acid, 230	acridine, 561
dimethyl acetate, 164	aldic acid, 549
ester, 164	aldine, 187, 466, 546
ethyl ester, 164	alizarin, 429
pthaleins, 366	azolon, 187
trimethyl ester, 164	azolons, 590
genic syntheses, 49	Quinene, 573
Pyromecazonic acid, 535	hydrone, 168
meconic acid, 522	Quinia-red, 232
mellitic acid, 246	Quinic acid, 299, 301, 550
mucic acid, 391, 450	Quinide, 301
Pyrone, 437, 522	Quinine, 571
carboxylic acid, 522	isatin, 261, 549, 551
dicarboxylic acid, 522	isatinic acid, 261
group, 442	lactam, 261
racemic anilide, 84	Quinite, 168, 294, 297
chloride, 83, 84	Quinizarin, 428
tritartaric acid, 451	
	Quinoanns, 1/2
Pyroxolon carboxylic ester, 405	Quinoanils, 172 Quinogens, 169
Pyroxolon carboxylic ester, 495 Pyrrodiazole, 427, 470, 511	Quinogens, 169
Pyroxolon carboxylic ester, 495 Pyrrodiazole, 437, 479, 511 dicarboxylic acid, 510	

662 INI	INDEX.	
Outpuling to 19th day	l Persuring of	
Quinoline, 73, 187, 545	Resaurine, 361	
acrylic acid, 546	Resazurin, 161	
aldehyde, 546, 549	Resin acids, 334	
betaine, 545	oils, 291	
carboxylic acid, 549	soaps, 334	
dicarboxylic acid, 550	Resins, 334	
group, 541	Resocyanine, 283	
iodmethylate, 545	Resorcin, 464	
ketones, 549	dialdehyde, 233	
lactic acid, 546	Resorcinol, 46, 159, 160	
oxalic acid, 546	benzeine, 360	
phenols, 546	diacetyl ester, 161	
red, 556	benzoate, 161	
yellow, 546	carbonic ester, 161	
Quinolinic acid, 536	methyl ether, 161	
Quinone, 75, 166, 167, 301, 404	monocarboxylic acids, 228	
anilinimide, 174	methyl ether, 161	
benzoylphenylhydrazone, 172	phthaleIns, 365	
chlorimide, 172	Resorcyl aldehyde, 220	
dianil, 80, 173	Resorcylic acid, 228	
chlorimide, 172	Resorufin, 161, 443, 580, 582	
methyl-anilinimide, 174	Retene, 415	
oxime, 67, 167, 168, 172	diphenic acid, 416	
carboxylic ester, 305	dodecahydride, 416	
haloids, 169	fluorene, 418	
homologues, 168	alcohols, 418	
imides, 115, 172	glycollic acid, 416	
monanil, 172	ketone, 416, 419	
monohydrazine, 168	quinone, 416	
monoxime, 167, 168, 172	Réuniol, 310	
nitrogen derivatives, 172	Rhamnose, 431	
phenol addition products, 168	Rhamnosides, 431	
imide, 173	Rhamnus frangula, 428, 432	
phenylhydrazones, 172	Rheinic acid, 428	
imide, 172	Rhodamine dyes, 154	
tetrabromide, 29 <b>7</b> carboxylic ester, 246	Rhodamines, 366	
hydro-tetracarboxylic ester,	Rhodanides, 106	
· · · · · · · · · · · · · · · · · · ·	Rhodinia soid 370	
307 Quinophthalone, 546	Rhodinic acid, 310	
oxaline dicarboxylic acid, 596	Rhodinol, 309	
	Rhodizonic acid, 171, 298	
oxalines, 96, 374, 397, 594, 596 oxalophenazine, 596	Ring alcohols, 294 amines, 295	
oxime, 152	formations, 19, 41	
Quinoyl, 167, 170	hexene, 292	
· ¿	etones, 296, 318	
	shaped chain, 30	
	strain, 444	
_	Roccella, 162	
R.	Rocellin, 400, 402	
REACTION of Liebermann, 141	Rosamine chloride, 360	
of Plugge, 142	Rosamines, 360	
Rearrangements of diazoamido compounds,		
109	constitution of, 356	
Red bergamot oil, 286	dyes, 351	
corallin, 361	sulphonic acid, 357	
oil, 355	Rose benzal, 366	
Regularities in substitution, 69	Rosemary oil, 315, 324	
Resacetophenone, 221	oil, 309	
,		

Scorzonera hispanica, 430

Rosindulines, 602 Rosolic acids, 359, 360, 361 Rubazonic acid, 488 Rubeanhydride, 130 Rubeanic acid, 499 Ruberythric acid, 427, 431 Rubia tinctorium, 427, 431 Rufigallic acid, 230, 429 Rufiopin, 429 Rufol, 423 Rule of Crum-Brown, 69 S. SACCHARIN, 134, 216 Safranines, 76, 96, 580, 600, 602 Safraninones, 603 Safranols, 603 Safran surrogate, 151 Safrinine, 443 Safrol, 268, 270 Safrosine, 366 Sage, 322 Salicin, 430 Salicylaldehyde, 463 amide, 225 amine, 217 anilide, 225 chloride, 224 Salicylic acid, 222, 280 methyl ester, 224 aldehyde, 218 Salicylide, 225 chloroform, 225 Salicyl-lactic acid, 253 Salicylo-nitrile, 225 phosphorous chloride, 224 Salicylous, 218 Saligenin, 217, 430 Salipyrine, 443, 488 Salix helix, 430 Salol, 224 Santoic acid, 432 Santonic acid, 432

Santonin, 400, 432

Sassafras officinalis, oil of, 270

Schaeffer's naphthol sulphonic acid, 406

Schaeffer's acid, 402, 403

Santous acid, 433 Saponaria officinalis, 431

Scammonin, 431

Schizomycetes, 251

Schöllkopf acid, 402

Saponin, 431

Roshydrazine, 359

Rosindols, 467 Rosindone, 602

Secondary naphthylamines, 396 phenylamines, 77 Sedanonic acid, 303 Selenazole, 508 group, 441 Selenophene, 447, 456 phthalide, 235 Selenoxene, 456 Selephene, 441 Semidine rearrangement, 118 Sesquiterpenes, 308 Shellac, 334 Shikimic, 299, **301** Shikimino-ki, 270 Shikimol, 270 Silico-benzoic acid, 133 tetraphenylamide, 81 Silver benzamide, 199 formanilide, 82 isatin, 472 Sinalbin, 226 Sinapan-propionic acid, 583 Siphonio elastica, 334
Six-membered heterocyclic compounds, Skatole, 466, 467 acetic acid, 468 carboxylic acid, 468 Sobreritrite, 325 Sobrerol, 325 Sobrerone, 325 Sodium acetanilide, 82 benzamide, 199 dibenzamide, 199 formanilide, 82 Solid green, 161, 355 Soluble blue, 359 Sophorine, 565 Sparteine, 567 Spiroylous, 218 Stilbazole, 530, 533 Stilbazonium base, 374 Stilbene, 178, 268, 370 carboxylic acid, 376 diamine, 372 bromide, 372 carboxylic acid, 252, 377 chloride, 372 glycol, 375 dibenzoate, 375 hydrate, 371 sulphide, 178 Storax, 266, 271, 274 Strain theory, 19 Strychnine, 256, 575 Stubb, 413 fat, 420 Styceric acid, 255

١

004 IND	BA.
Stycerine, 248	Sulphobenzoic anil, 216
Styphnic acid, 161	camphoric acid, 332
	camphylic acid, 332
Styracine, 275	carbanilamide, 87
Styrene, 49	
Styrolene, 254, 255, 266	carbanile, 89
alcohol, 247	cinnamic acid, 278
dichloride, 247	hydraziacetic ester, 445
homologues of, 268	hydrazine-cinnamic acid, 277
Styrolenes containing substituents in the	isophthalic acid, 242
side group, 267	Sulphones, 134, 139
substituted in the benzene nu-	Sulphonic acids, 133, 398
cleus, 267	of phenol, 156
Styrone, 266, 271	phosphazobenzene chloride, 81
Styrylamine, 271	phthalic acids, 241
pyridine, 533	quinolines, 547
Suberan carboxylic acid, 28	succinyl, 438, 441
Subcrane, 28	terephthalic acid, 243
Suberone, 28	Sulphovinic acid, 506
Suberyl alcohol, 28	Sulphoxylphenyl-p-sulphoxylphenylhydra
Suberylene, 28	zono-pyrazolon-carboxylic acid, 490
glycollic acid, 29	Sulphurized azo-dyes, 137
Substantive dyes, 338	Sulphydrobenzothiazole, 157, 508
Substituted anthracenes, 423	benzoxazole, 153
anthraquinones, 425	derivatives, 498
aromatic mono-carboxylic acids,	Sultams, 399
209	Sultones, 403
benzoyl formic acids, 258	Sylvic acid, 334
fluoresceins, 366	Sylvan, 448
naphthalenes, 395	Sylvestrene, 312
naphthoic acids, 408	Symmetrical azo-bodies, 112
naphthols, 401	constitution, 30
naphthoquinones, 404	structure, 33
naphthylamines, 397	Synbenzaldoxime-N-methyl ether, 186
Succinanil, 91	phenylglyoxylic acid oxime, 258
Succinanilic acid, 91	Syringaic acid, 231
Succinic acid, 465	Syringia vulgaris, 430
anhydride, 437, 441	
phenylhydrazilic ester, 129	Syringin, 430
Succinimide, 438, 441, 462	Т.
Succino-rhodamine, 367	
succinic acid, 244, 305	TARULAR OXYLEPIDENE, 381
diethyl ester, 305	Tanacetene, 312, 319
methyl ester, 305	Tanacetophorone, 26
ester, 307	Tanacetum vulgare, 319
Succinyldiphenylhydrazide, 129	Tanacetyl alcohol, 316
phenylhydrazine, 129	Tannic acid penta-acetate, 231
Sulphamine benzoic acid, 216	acids, 23I
Sulphanilic acid, 137	Tannin, 231
Sulphanilide, 80	of coffee, 232
Sulphazides, 119	of oak, 232
hydrylchlorstyrene, 465	Tartrazine, 490
Sulphinic acids, 134, 138	Tartrazinic acid, 490
Sulpho-acid indols, 468	Taurine, 137
acids, 133	Teraconic acid, 324
benzene azophenol, 156	crylic acid, 324
disulphide, 139	Terebic acid, 319, 324
sulphide, 139	Terephthalaldehyde, 233
benzide, 140	dioxime, 233
	aldebydic acid, 238
benzoic acid, 216	

į

Terephthalic acid, 243
phthalophenone, 351 Terpadiënes, 309
Terpan, 309
group, 310
Terpene alcohols, 308 ketones, 308
Terpenenes, 312
Terpenes, 290, 293, <b>307</b> Terpenogen group, 309
Terpenylic acid, 324
Terpine, 314 hydrate, 310, 314
Terpinene nitrosite, 312
Terpineol, 316
Terpinolene, 312, 317 Tertiary alcohols, 31
amyl phenol, 145
butyl phenol, 145 carvomenthol, 314
menthol, 314
naphthylamines, 396
phenylamines, 77 Tetra-alkylic para-phenylene - diamines,
116
amidobenzene, 97 diphenyl-azo-phenylene, 95
phenylene-bisazobenzene,116
benzyl urea, 180
brombenzoquinone, 167 cyclohexandion, 297
dichlorfluorescein, 366
fluoresceIn, 366 phenolphthalein, 364
diethyl ethers,
365 mono - ethers,
365
oxime, 365
quinone, 163 terephthalic acid, 243
Tetrabromtetrachlorfluorescein, 366
thiophene, 454 xylene, 233
carboxylic acids, 265
chlorbenzoquinone, 167
hydrindone, 387, 393 ketodihydrobenzene, 299
phenol, 149
n-phenylpyrrol, 459 phthalic acid, 241
pyridine, 533
pyrrol, 459
quinone, 45, 163 terephthalic acid, 243
tetraketohexamethylene, 170,
297 thiodiphenylamine, 584
phene, 454
11—56

```
Tetrachlortriketopentamethylene, 170
          xylene oxide, 232, 463
Tetracid methan alcohols, 316
     derivatives, formation of, 69
     ethyl benzene, 57
           phenosafranine, 603
     hydric phenols, 166
     hydroacids, 47
           benzene, 293
                    dibromide, 293
                    nitrosate, 293
                    nitroso chloride, 293
           benzoic acid, 300
           carbazole, 468, 477
carboxylic acid, 478
           carveol, 314
           carvone, 318
           carvylamine, 317
           dicarboxylic acids, 303
             oxyterephthalic acid, 244, 305
             pentene tribromide, 312
             phenyl, 335
furfurane, 451
           fenchene, 324
           glyoxalidines, 499
           isoquinoline, 557
keto-quinazoline, 181
           methyl-phenyl-furfurane, 451
          naphthalene, 411
derivatives, 411
           naphthoic acids, 413
           naphthol, 412
           naphthoquinolines, 553
                   quinone, 412
           naphthylamines, 393, 412
           naphthylene diamine, 412
                        dicarboxylic acid,
                          413
                        glycol, 392
                        oxide,
                                411, 412,
                    phenol, 412
          naphtinolin, 379, 558
nicotinic acid methyl betaine,
             565
           oxyterephthalic acid, 304
           phenol, 295
           phenyl dimethyl pyrazole, 483
           phthalazine, 586
           phthalic acids, 303
           picoline, 538
           prehnitic acid, 307
           pyrazole, 480
                     derivatives, 490
           pyro-mellitic acid, 306
           pyrrol, 461
           quinaldine, 191, 470, 551
            quinezoline, 591
             quinoline, 465, 545, 552
```

Tetrahydroquinone, 297	Tetramidoanisol, 154
quinoxaline, 596	diphenyl, 338
terephthalic acid, 303	Tetramines, 97
thiophene - dicarboxylic acid,	nitroanthraquinone, 432
438, 456	benzophenone, 347
thioquinazoline, 181	diphenyl acetic acid, 369
toluene, 293	methane, 393
toluic acid, 301	naphthalenes, 396
iodofluoresceln, 366	phenol, ISI
phthalic acid, 241	oxyanthraquinone, 429
pyrrol, 459	benzaldehydes, 220
terephthalic acid, 243	benzene, 166
tetrachlorfluorescein, 366	tetraacetyl ester, 166
methoxybenzyl isoquinoline, 576	biphenyls, 339
diphthalyl, 376	cinnamic acid, 283
methylamidophenthiazimium chlo-	diphenyl acetic acid, 369
ride, 584	naphthalene, 404
apionol, 166	quinone, 170
benzenes, 55	phenylaldine, 593
benzoic acids, 196	crotolactone, 381
diamido-azoxy-benzene, 112	dihydrop <b>yridazine, 483, 585</b>
benzhydrol, 344	phenylene-ethylene dioxide, 524
benzophenone, 78, 348	furfurane, 415
diphenyl methane ox-	ethane, 378
ide, 524	ethane dicarboxylic acid, 378
diphenyl phthalide,	ethylene, 378
363	furfurane, 449
imidobenzophenone	guanidine, 89
hydrochloride, 348	hydrazine, 117
thiobenzophenone,	methylene glycol, 378
348	pyrazine, 593
triphenyl carbinol,	pyridines, 533
354	pyrrol, 459
triphenyl methane,352	silicon, 133
triphenyl methane car-	succinic acid, 378
boxylic acid, 362	tetrazone, 131
xanthene, 524, 525	thiophene, 454
xanthone, 525	thiurea, 87
dipyrrol, 467, 468	urea, 85
methylene carboxylic acid, 24	salicylide, 225
· diglyoxylic acid, 24	tolyloxamide, 91
piperidine, 453	Tetrazine group, 442
sulphide, 442	Tetrazines, 606
group, 24	Tetrazinic acid, 490
imide, 480	Tetrazole group, 441
pyrrolidine, 438	Tetrazoles, 437, 480, 519
imine, 461	Tetrazolium, 520
oxide, 437, 444	Tetrazones, 64, 121, 131
indol, 467, <b>468</b>	Tetrazylazoimide, 520
methyl benzoxypiperidine car-	hydrazine, 520
boxylic ester, 540	Tetroxy terephthalic ester, 306
paraleucaniline, 358	Thebaine, 576
phenols, 145	Thebenine, 576
phenylglyoxylic acid, 259	Thebenol, 576
piperazine, 594	Thetine, 440
pyrazine, 593	Thiacetamide, 504
pyrazole, 482, 483	Thialdines, 608
pyridine, 532	Thialdolaniline, 79, 440
violet, 358	Thianthrene, 160

Thiazines, 582	Thionylamines, 80
hiazole, 437	anilines, 73, 80
carboxylic acids, 506	benzene, 139
group, 441, 443	benzidine, 337
hiazoles, 479, 480, 502, 504, 511	bromaniline, 80
hiazoline-mercaptan, 506	chloraniline, 80
hiënone, 455	nitraniline, 80
hienyl acrylic acid, 455	phenylhydrazone, 125
diphenyl methane, 454	toluidine, 80
glyoxylic acid, 455	oxybiazolines, 516
indol, 468	phenaldehyde, 455, 465
methyl ketone, 455, 468	Thiophene, 48, 257, 437, 438, 441, 443,
phenyl ketone, 455	447, 452, 456, 462, 472,
sulphydrate, 455	479
triphenyl methane, 454	alcohol, 455
Thioacetanilide, 83	carboxylic acids, 455
aldol aniline, 79	dicarboxylic acid, 455
anilides, 83	of crystallization, 351
anilines, 158	sulphonic acids, 455
anisol, 158	tetracarboxylic methyl ester,
benzaldehyde, 184	456
benzamide, 204	phenin, 655
benzanilide, 204	phenol, 156
benzimidazoline, 502	ethyl ether-sulphonic acid,
benzoic acid, 199	105
benzophenone, 346	sulphonic acid, 105
benzoxazole, 504	phenyl acetal, 157
biazole group, 441	acetone, 157
biazoles, 517	amine, 157
biazolines, 88, 479, 480, 517	phthalic anhydride, 240, 463
carbanilic ethyl ester, 86	phthalide, 235, 463
carbonyl-thiocarbanilide, 446	resorcinol, 161
ureas, 446	salol, 224
chlorstyrolene, 269	tetrahydroglyoxalines, 499
coumarin, 281	quinazolines, 591
coumazones, 581	tolene, 454
coumothiazone, 583	toluidine, 158
cresol, 157	triazoles, 480, 518
cumazone, 181	urazole, 514
cumothiazone, 181	Thioxanthenes, 526
cymene, 145, 157	Thioxanthone, 526
diazines, 608	Thioxenes, 454
azoles, 479, 480	Thioxycyanidine, 605
glycol-anilic acid, 84	Three-membered heterocyclic substances,
glycollic anhydride, 442	440, 444 Thuismenthol 374
phenylamine, 80, 158, 160, 583 imides, 158	Thujamenthol, 314
flavin, 508	menthone, 319
formanilide, 83	oil, 319 Thujen, 312
ketotetrahydroquinazoline, 592	Thujonamine, 317
methyl phenyl-carbaminate, 87 monazoles, 504	Thujone, 319 Thujyl alcohol, 316
naphthene, 465	Thymodialdehyde, 233
naphthol, 404	Thymotl, 169
hionbenzoic acid, 199	Thymol, 144, 318
essal, 370, 454	Thymooxycumic acid, 226
<b>hionia</b> e, 584	quinone, 144, 169
dyes, 80	Thymotic acid, 226
Thiomp1, 584	Thymotin alcohol, 218
	/

	•
Thymotin aldehyde, 219	Tolyl-phthalide, 349
Thymus vulgaris, 144	phosphor chloride, 132
Tin diphenyl chloride, 133	pyrazole, 483
tetraphenyl, 133	sulphamic acid, 80
Tolallyl sulphide, 375	tetrazole, 520
Tolane, 368, 371	trianilidophosphonium chloride,
dichloride, 375	132
sulphide, 375, 444	Tolypyrine, 443, 488
tetrachloride, 375	Tonka bean, 281
Tolazone, 587	Trans-benzene hexachloride, 293
Tolidine disulphonic acid, 339	Triacetyl benzene, 233
Tolidines, 118, 338	gallic acid, 230
l'olimidazole-carboxylic acid, 501	acid menthan alcohols, 315
Tolu balsam, 274	amido-azobenzene, 95, 116
benzylamine, 179	benzoic acid, 214
Toluene, 49, 52, 53	cyanidine, 605
azo-naphthalene, 398	diphenyl, 338
disulphonic acid, 136	tolyl carbinol, 355
sulphamide, 135	methane, 353
sulphinic acid, 139	phenol, 154
sulphonic acids, 135	phloroglucin, 165
hydroquinone, 70, 163	toluene, 97
Toluic acid, 191, 194, 394	triphenyl-acetic nitrile, 369
aldehyde, 184	amine, 80
anhydride, 198	carbinols, 355
formaldehyde, 249	methanes, 352
idines, 62, 75	amines, 97
Tolunitriles, 202	azine group, 442
phenazine, 598	azines, 604
piaselenol, 518	azole carboxylic acid, 513
quinaldine, 546	azoles, 479, 480, 504, 511
quinone, 152, 168	azolons, 513
dioxime, 70, 172	azsulpholes, 441, 480, 518
quinoxaline, 596	benzal-diamine, 184
safranine, 603	benzamide, 199
tolyl-dihydrotriazine, 606	benzoyl hydroxylamine, 207
Toluylazimido ethoxy benzene, 511	methane, 379
chloride, 198	benzylamine, 178
Toluylene, 370	hydroxylamine, 180
acetamidine, 501	urea, 180
blue, 174	bromaceto-benzoic acid, 265
diamines, 05 glycol, 371	aniline, 92
hydrate, 371	fluorane, 365 glyoxaline, 498
red, 95, 443, 580	hemimellithene, 63
	mesitylene, 63
group, 599 urea, 502	phenylazocarboxylic acid, 104
Tolyl-acetic acid, 196	pseudocumene, 63, 292
acetonitrile, 203	cumenol, 149
acrylic acid, 278	pyrogallol, 164
azimidotoluene, 511	quinone, 163
carbinol, 177	resorcinol, 161
glyoxylic acid, 250	terpan, 312
hydrazines, 120	thiophene, 454
hydrazine sulphonic acid, 135	carbazole carbinol, 359, 477
hydroxylamines, 70	carboxylic acids, 245, 265
isocyanides, 83	chloraceto-benzoic acid, 265
methyl ketone, 56	pentachlor-butyric actid, 46
phenyl ketone, 345	amido-pyridine, 533
phenyi ketone, 343	

oraniline, 92 T 74 benzene hexachloride, 293 cyanidine, 605 dinitrobenzene, 68 ethidine acetophenone, 288 isoquinoline, 555 methylphenyl orthophosphoric acid chloride, 224 naphthalenes, 395 orcin, 162 oxymethyl coumarilic acid, 464 pentene dioxycarboxylic acid, 143 phenol, 149 phenomalic acid, 45 phosphanil, 81 pyridine, 533 pyrogallol, 164 quinoline, 91, 547 quinone, 163 tetraketo-hexamethylene, 170, 297 triketopentamethylene, 170 vinyl benzoic acid, 393 derivatives, formation of, 69 ethyl cyanidine, 604 gallic ether acids, 230 oxyhydroquinone ether-acid, 231 phenyl silicide, 133 pyrogallol carboxylic acid, 230 furyldihydroglyoxaline, 499 gonelline, 565 hydrazine derivatives, 359 hydric aromatic alcohols, 232 phenols, 164 iodstyrolene, 267 ketocyclopentan dicarboxylic ester, 28 hexamethylene, 165 dicarboxylic ester, 306 hydrindene, 388 piperidine, 535 pyrolidone, 462 ketones, 233, 250 ketotetrahydroquinoline, 549 mellitic acid, 245 mesic acid, 55, 136, 245 trimethyl ester, 245 methyl amidophenol, 154 ammonium phenol, 153 benzoic acid, 195 cyclohexane, 298 dihydroquinoline, 471 methylene, 22 benzamidine, 204, 205 carbanilide, 85 carboxylic acids, 22 diamine derivatives, 482 dicarboxylic acid, 23

Trimethylene imide, 438, 440, 446 oxide, 437, 440, 446 piperylium bromide, 540 sulphide, 438 tricarboxylic acid, 23 ethyl benzene, 56 gallic ether acids, 230 glyoxaline, 498 hexamethylene, 292 indol, 468 indolinon, 471 isoxazole, 494 ketohexamethylene, 296 hexene, 298, 307 oxyindolin, 471 oxytetrahydronaphthylene ammonium hydroxide, 412 piperazine, 594 pyrazine, 593 pyrazole, 482 pyrazoline, 486 pyridine, 532 dicarboxylic acid, 537 quinolines, 546 salicylic aldehyde, 219 thiazole, 505 tricarballylic acid, 333 phenyl-pararosaniline, 359 nitraniline, 93 nitrobenzenes, 67 butyl toluene, 68 chlorbenzene, 67, 150 cresol, 151 diethyl hydroquinone, 164 phenyl tolyl methane, 351 naphthalenes, 396 naphthol, 401 oxytoluic acid, 226 phenol, 150 phenyl acetoacetic ester, 260 malonic ester, 262 methane, 351 phloroglucin, 165 pseudocumene, 68 resorcinol, 161 diethyl ester, 161 nitroso phloroglucin, 165 trimethyl benzene, 68 phenyl carbinol, 353 nitroxylene, 68 nitroxylidine, 93 oxy alcohol acids, 256 anthraquinone carboxylic acid, 429 anthraquinones, 428 aurine, 361 benzaldehydes, 220 cinnamic acid, 283 dicarboxylic acida, 244 phenyl tolyl carbinol, 361



670

•	
Trioxyhexahydrocymene, 315, 316	Triphenyl phosphine, 132
hexamethylene, 165, 295	phosphin-oxide, 132
methylanthraquinone, 428	phosphorbetaine, 446
isocarbostyril, 557	propers and
naphthalenes, 404	pyrazole, 483
phthalic acid, 244	perceoline 486
pyridines, 535	pyridazine, 585
quinoline, 549	rosaniline, 80
	hydrochloride, 35
triphenyl methane, 359, 360	stibine, 133
manthone, 525	tetrazolium hydroxide, 206
phenazine oxazine, 604	
benzene, 189	hydroglyoxaline, 499
dioxazine, 582	thiazole, 505 thiurea, 87
phenyl acetic acid, 369	triazole, 512
acrylic ester, 378	
amine, 71, 80	brompyrazoline, 486
arsine, 132	urea, 85
benzene, 342	vinyl alcohol, 377
benzyl-glyoxaline, 496	Tripyrrol, 457
biuret, 86	quinolyl methane, 547
bromethanon, 377	quinoyl, 171, 297
methane, 353	resorcinol, 161
pyrazole, 483	sazo-compounds, I12
carbinol, 353	thioaldehyde, 442
amine, 353	benzaldehyde, 184
carboxylic acid, 363	carbonic ethylene ester, 478
carboxylic acid lac-	cinnamic aldehyde, 272
tone, 362	vanillin, 220
chloride, 353	toluene sulphonamide, 136
phenylamine, 353	Tropa-cocaine, 569
chlormethane, 353	Tropæoline, 138
crotolactone, 381	Tropæoline Y, 156
cyanidine, 604	Tropic acid, 252
urate, 89	Tropelnes, 567
urtriamide, 90	Tropine, 253, 541, 567, 568
dihydroglyoxaline, 184, 497,	carboxylic acid, 570
499	group, 567
pyrazine, 585	True terpenes, 308
ethane, 377	Truxillic acids, 569
ethanon, 377	Turpentine oil, 311, 322
ethoxyethanon, 377	Twin nuclei, 29
furfurane, 449	Tyrosine, 253
glyoxaline, 497, 498	
guanidine, 87, 88	
isocyanurate, 89	บ.
melamine, 89, 90	
phenylium iodide, 78	ULEXINE, 565
melamine, 90, 351	Umbellic acid, 282, 283
methane carboxylic acid 361,	Umbelliferone, 160, 283, 463
362	Unsymmetrical azo-bodies, 112
group, 351	Uracil derivatives, 589
potassium, 351	Uramido-benzoic acid, 212
methylamine, 353	Urazine, 607
ethane, 378	Urazoles, 514
pyrazolidine, 490	Urea, 253
phenylol methane, 360	chlorides, 85
osotriazole, 509	Ureldes, 86
oxyethanon, 377	Ureines, 374, 499
pararosaniline, 359	Urine indican, 469

V.

**HYDROQUINONE, 221** lactam, 438 lactone, 437 acetophenone, 250 : acid, 228 1, 219, 270, 272 nic acid, 270 oxime, 220 l alcohol, 218 ies, 334 : acid, 228, 270 l, 159 yl-carboxylic acid, 259, 270 m alkaloids, 575 amine, 317 a blue, 348 orange, 151 nic acid, 23 misol, 269 enzene, 49, 266 enzoic acid, 273 liacetonalkamines, 540 ruaiacol, 269 henol, 269 henyl acetic acid, 273 yridine, 533 rimethylene, 22 iline, 356 acid, 382

w.

R BLUE, 359

Wool-black, 400 Wormwood oil, 319

X. XANTHENES, 410, 524 Xanthochelidonic acid, 522 gallol, 164 Xanthogen anilide, 86 Xanthogenic esters, 105 Xanthone, 348, 362, 524 Xanthoxalanil, 462 Xanthydrol, 524 ether, 524 Xenylamine, 336 Xylene, 49, 52, 54, 266 alcohol, 232 dichlor-dimalonic esters, 265 sulphonic acids, 136 sulphide, 232 sulphonic acids, 136 tetrachloride, 233 Xylenols, 144, 149, 298 Xylic acid, 191, 195 Xylidic acid, 243 Xylidines, 76 Xylonitrile, 202 quinone, 169 Xylorcin, 161 Xylylamine, 179 Xylylene alcohols, 232 diamines, 95 dimalonic tetra-ethyl esters, 265 imine, 463 sulphide, 463

Y.

YELLOW CORALLIN, 361 Ylangol, 310

Xylyl glyoxylic acid, 259





# $MEDICAL \\ BOOKS$

NOTE SUBJECT INDEX
P A G E S I X

THERE HAVE BEEN SOLD MORE
THAN 165,000 COPIES OF
GOULD'S DICTIONARIES

SEE PAGES
12 AND 13

P. BLAKISTON'S SON & COMPANY

Publishers of Medical and Scientific Books

1012 WALNUT STREET, PHILADELPHIA

## Montgomery's Gynecology

#### New Edition-Just Ready

A modern comprehensive Text-Book. By EDWARD E. MONTGOMERY, M.D., Professor of Gynecology in Jefferson Medical College, Philadelphia; Gynecologist to the Jefferson and St. Joseph's Hospitals, etc. Second Edition, Revised and Enlarged. 539 Illustrations, many of which are from original sources. Octavo. Cloth, \$5.00; Leather, \$6.00

** This is a systematic modern treatise on Diseases of Women. The author's aim has been to produce a book that will be thorough and practical in every particular. The illustrations, nearly all of which are from original sources, have for the most part been drawn by special artists who, for a number of months, devoted their sole attention to this work. The present edition has been thoroughly revised.

"The book is one that can be recommended to the student, to the general practitioner—who must sometimes be a gynecologist to a certain extent whether he will or not—and to the specialist, as an ideal and in every way complete work on the gynecology of to-day—a practical work for practical workers."—The Journal of the American Medical Association.

## Byford's Gynecology

Third Revised Edition

#### A MANUAL FOR STUDENTS AND PHYSICIANS

By HENRY T. BYFORD, M.D., Professor of Gynecology and Clinical Gynecology in the College of Physicians and Surgeons of Chicago; Professor of Clinical Gynecology, Women's Medical School of Northwestern University, and in Post-Graduate Medical School, etc. Third Edition, Enlarged. 363 Illustrations, many of which are from original drawings and several of which are Colored. 12mo.

Cloth, \$3.00

[&]quot;As a book to help the student to quickly review what ought to be gotten up, so as to be prepared for the early examination, it is of great service. Such a book would also make a most excellent text-book for the college class room."—Virginia Medical Semi-Monthly, Richmond.

#### By JAMES TYSON, M.D.,

Professor of Medicine, University of Pennsylvania, Physician to the Pennsylvania Hospital, etc.

#### The Practice of Medicine. Third Edition.

A Text-Book for Physicians and Students, with Special Reference to Diagnosis and Treatment. With Colored Plates and many other Illustrations. Third Edition, Revised and Enlarged. 134 Illustrations. 8vo. 1240 pages.

Cloth, \$5.50; Leather, \$6.50

*** This edition has been entirely reset from new type. The author has revised it carefully and thoroughly, and added much new material and new illustrations.

"We are firmly convinced that at the present time Dr. Tyson's book on Practice can be most heartily commended to both the practitioner and student as a sate, reliable, and thoroughly up-to-date guide in the practice of medicine."—The Therapeutic Gazette.

"The clinical descriptions are clear and full, and the methods of treatment described are those generally recognized as being the most modern and satisfactory."—The London Lancet.

## Guide to the Examination of Urine. Tenth Edition.

For the Use of Physicians and Students. With Colored Plate and Numerous Illustrations Engraved on Wood. Tenth Edition, Revised, Enlarged, and in many parts entirely rewritten. Cloth, \$1.50

- *** A French translation of this book has been published in Paris.
- "The book is probably more widely and generally known and appreciated than any of its similars in subject and scope."—New York Medical Journal.
- "The book is a reliable one, and should find a place in the library of every practitioner and student of medicine."—Boston Medical and Surgical Journal.

## Handbook of Physical Diagnosis. Fourth Edition.

Revised and Enlarged. With two Colored Plates and 55 other Illustrations. 298 pages. 12mo. Cloth, \$1.50

"Like everything else emanating from this distinguished author this little book is replete with practical information from beginning to end."—The Chicago Medical Recorder.

"The author approaches his subject from a practical point of view and the little work will prove a good friend to the student."—
The American Journal of the Medical Sciences.

#### NEW THIRD EDITION—NOW READY

## MORRIS' ANATOMY

Rewritten-Revised-Improved

#### WITH MANY NEW ILLUSTRATIONS

Out of 102 of the leading medical schools 60 recommend "Morris." It contains many features of special advantage to students. It is modern, up-to-date in every respect. It has been carefully revised, the articles on Osteology and Nervous System having been rewritten. Each copy contains the colored illustrations and a Thumb Index.

Octavo. With 846 illustrations, of which 267 are printed in colors.

CLOTH, \$6.00; LEATHER, \$7.00

"The ever-growing popularity of the book with teachers and students is an index of its value, and it may safely be recommended to all interested."—From *The Medical Record*, New York.

"Of all the text-books of moderate size on human anatomy in the English language, Morris is undoubtedly the most up-to-date and accurate."—From The Philadelphia Medical Journal.

## McMurrich—Embryology

#### THE DEVELOPMENT OF THE HUMAN BODY

With 270 Illustrations

A Text-Book for Medical Students. By J. Playfair McMurrich, Professor of Anatomy, Medical Department, University of Michigan. 527 pages. Cloth, \$3.00

#### NINTH EDITION

## POTTER'S MATERIA MEDICA, PHARMACY, AND THERAPEUTICS

#### An Exhaustive Handbook

Including the Action of Medicines, Special Therapeutics of Disease, Official and Practical Pharmacy, and Minute Directions for Prescription Writing, etc. Including over 650 Prescriptions and Formulæ. By Samuel O. L. Potter, M.A., M.D., M.R.C.P. (Lond.), formerly Professor of the Principles and Practice of Medicine, Cooper Medical College, San Francisco; Major and Brigade Surgeon, U. S. Vol. Ninth Edition, Revised and Enlarged. 8vo.

With Thumb Index in each copy.

Cloth, \$5.00; Leather, \$6.00

*** This is the most complete and trustworthy book for the use of students and physicians. Students who purchase it will find it to contain a vast deal of information not in the usual text-books arranged in the most practical manner for facilitating study and reference. It cannot be surpassed as a physician's working book.

#### WHITE AND WILCOX. Materia Medica, Pharmacy, Pharmacology, and Therapeutics. Fifth Edition.

A Handbook for Students. By W. Hale White, M.D., F.R.C.P., etc., Physician to, and Lecturer on Materia Medica and Therapeutics at, Guy's Hospital, etc. Fifth American Edition, Revised by Reynold W. Wilcox, M.A., M.D., I.L.D., Professor of Clinical Medicine and Therapeutics at the New York Post-Graduate Medical School and Hospital; Visiting Physician, St. Mark's Hospital; Assistant Visiting Physician, Bellevue Hospital. 12mo.

Cloth, \$3.00; Leather, \$3.50

#### SUBJECT INDEX.

Gould's Medical Diction	ari	es,	_	Pag	ges 12, 1	3
Morris' Anatomy, -	-	-	-	-	Page	4
Compends for Students.	-	-	-	•	Page 2	7

SUBJECT. PAGE	SUBJECT. PAGE
Alimentary Canal (see Sur-	Medical Jurisprudence 18
gery) 24	Mental Therapeutics 8
Anatomy	Microscopy
Anesthetics	Milk
Autopsies (see Pathology) 20	Miscellaneous 18
Bacteriology 8	Nervous Diseases 19
Bandaging (see Surgery) 24	Nose 25
Blood, Examination of 8	Nursing 20
Brain	Obetetrics 20
Bright's Disease 26	Ophthalmology 14
Chemistry. Physics 9	Organotherapy 18
Children, Diseases of 11	Osteology (see Anatomy). 7
Climatology 19	Pathology 20
Clinical Charts 25	Pharmacy 21
Compends 27	Physical Diagnosis 11
Consumption (see Lungs). 16	Physical Training 17
Cyclopedia of Medicine 13	Physiology 22
Dentistry 11	Pneumotherapy 19
Diabetes (see Urin. Organs) 25	Poisons (see Toxicology) 18
Diagnosis	Practice of Medicine 22
Diagrams (see Anatomy). 8	Prescription Books (Phar-
Dictionaries, Cyclopedias. 12	macy) 21
Diet and Food	Refraction (see Eye) 14
Disinfection 16	Rest 19
Dissectors 7	Sanitary Science 16
Ear 14	Serum-Therapy 17
Electricity 14	Skin 23
Embryology 7	Spectacles (see Eye) 14
Emergencies 24	Spine (see Nervous Dis-
Eye 14	eases)
Fevers	Stomach 23
Food	Students' Compends 27
Formularies 21	Surgery and Surgical Dis-
Gynecology	eases 24
Hay Fever	Technological Books 9
Heart	Temperature Charts 25
Histology	Therapeutics 17
Hydrotherapy 19	Throat
Hygiene	Toxicology
Hypnotism 8	Tumors (see Surgery) 24
Insanity	U. S. Pharmacoposia 22
Intestines	Urinary Organs 25
Latin, Medical (see Phar-	Urine
macy)	Venereal Diseases 26
Life Insurance 19	
Lungs	Veterinary Medicine 25 Visiting Lists, Physicians'.
	(Send for Circular.) Water Analysis
Materia Medica	
Mechanotherapy 17	Women. Diseases of 15

Self-Examination for Medical Students. 3500 Questions on Medical Subjects, with References to Standard Works in which the correct replies will be found. Together with Questions from State Examining Boards. 3d Ed. Paper Cover, 10 etc.

SPECIAL NOTE.—The prices given in this catalogue are net; no discount can be allowed retail purchasers under any consideration. This rule has been established in order that everyone sideration. will be treated alike, a general reduction in former prices having been made to meet previous retail discounts. Upon receipt of the advertised price any book will be forwarded by mail or express, all charges prepaid.

#### ANATOMY. EMBRYOLOGY.

MORRIS. Text-Book of Anatomy. Third Revised and Enlarged Edition. 846 Illustrations, 267 of which are printed in colors. Thumb Index in Each Copy. Cloth, 86.00; Leather, \$7.00 "The ever-growing popularity of the book with teachers and students is an index of its value."—Medical Record, New York.

BROOMELL. Anatomy and Histology of the Human Mouth and Teeth. 2d Edition, Enlarged. 337 Illus. Cloth, \$4.50 DAVISON. Mammalian Anatomy. With Special Reference to the Cat. 108 Illustrations. \$1.50

EAVER. Surgical Anatomy. A Treatise on Anatomy in its Application to Medicine and Surgery. With 499 very handsome full-page Illustrations Engraved from Original Drawings made by special Artists from dissections prepared for the purpose. Three vols. By Subscription only. DEAVER.

Half Morocco or Sheep, \$30.00; Half Russia, \$33.00

Anatomy of the Central Nervous System. With 271 Illustrations, many of which are original. Cloth, \$6.00 HEATH. Practical Anatomy. 9th Edition. 321 Illus. HOLDEN. Anatomy. A Manual of Dissections. Revised by A Hawson, M.B., Demonstrator of Anatomy, Jefferson Medical College, Philadelphia. 320 handsome Illustrations. 7th Ed. In two compact 12mo volumes. 850 pages. Large New Type. Vol. I. Scalp—Face—Orbit—Neck—Throat—Thorax—Up-

per Extremity.

Vol. II. Abdomen—Perineum—Lower Extremity—Brain—
Eye—Ear—Mammary Gland—Scrotum—Testes \$1.50

OLDEN. Human Osteology. Comprising a Description of the Bones, with Colored Delineations of the Attachments of the Muscles. The General and Microscopical Structure of Bone and its Development. With Lithographic Plates and numerous Illustrations. 8th Edition. \$5.25 HOLDEN.

HOLDEN. Landmarks, Medical and Surgical. 4th Ed. HUGHES AND KEITH. Dissections. With 527 Colored Plates

and other Illustrations. In three parts.
I, Upper and Lower Extremity.
II, Abdomen—Thorax.
III, Head—Neck—Central Nervous System. \$3.00 \$3.00

\$3.00

LAZARUS-BARLOW. Pathological Anatomy. 21 Plates and 171 other Illustrations.

McMURRICH. Embryology. The Development of the Human Body. 276 Illustrations. \$3.00

8-28-04

ARSHALL. Physiological Diagrams. Eleven Life-Size Colored Diagrams (each seven feet by three feet seven inches). Designed for Demonstration before the Class.

In Sheets, Unmounted, \$40.00; Backed with Muslin and Mounted on Rollers, \$00.00; Ditto, Spring Rollers, in handsome Walnut Wall Map Case, \$100.00; Single Platee—Sheets, \$500.00; Single Platee—Sheets, Spring Rollers, Spring MARSHALL

\$5.00; Mounted, \$7.50. Explanatory Key, .50. Purchaser must pay freight charges.

MINOT. Laboratory Text-Book of Embryology. 218 Illustra tions.

OTTER. Compand of Anatomy, Including Visceral Anatomy. 7th Edition, Revised and Enlarged. Numerous Tables, 16 Plates and 188 other Illustrations. \$1.00; Interleaved, \$1.25 POTTER. TOMES. Dental Anatomy. 6th Edition. In Press. WILSON. Anatomy. 11th Edition. 429 Illus., 26 Plates. \$5.00 YUTZY. Guide to the Dissection of the Human Body. Based on Morris' Anatomy. Paper Cover, .25

#### BACTERIOLOGY.

CONR. Agricultural Bacteriology. Including the Study of Bacteria as relating to Agriculture, Soil, Dairy and Food Products, Sewage, Domestic Animals, etc. Illustrated. \$2.50 CONN. Bacteria in Milk and Its Products. Designed for Students of Dairying, Boards of Health, Bacteriologists, etc. Illustrated. \$1.25 Illustrated.

EMERY. Bacteriological Diagnosis. 2 Colored Plates and 32 other Illustrations. \$1.50

HEWLETT. Manual of Bacteriology. 75 Illustrations. Second Edition, Revised and Enlarged. \$4.00

HEWLETT. Serum-Therapy. Bacteriological Therapeutics and Vaccines. Illustrated. \$1.75

SMITH. Laboratory Exercises in Bacteriology. A Handbook for Students. Illustrated. \$1.50

WILLIAMS. Bacteriology. A Manual for Students. 99 Illustrations. 3d Edition, Revised. \$1.50 \$1.50

#### BLOOD, Examination of.

DA COSTA. Clinical Hematology. A Practical Guide to the Examination of the Blood, with Reference to Diagnosis. Six Colored Plates and 48 other Illus. Cloth, \$5.00; Sheep, \$6.00

#### BRAIN AND INSANITY (see also Nervous Diseases.)

BARR. Mental Defectives. Illustrated. In Press. BLACKBURN. A Manual of Autopsies. Designed for the Use of Hospitals for the Insane. Illustrated. \$1.25 \$1.75 CHASE. General Paresis. Illustrated. DERCUM. Mental Therapeutics, Rest, Suggestion. See Cohen, Physiologic Therapeutics, page 17. GORDINIER. The Gross and Minute Anatomy of the Central Mervous System. With full-page and other Illus. \$6.00 IRELAND. The Mental Affections of Children. 2d Ed. \$4.00 LEWIS (BEVAN). Mental Diseases. A Text-Book having Special Reference to the Pathological Aspects of Insanity. 26 Lithographic Plates and other Illustrations. 2d Ed. \$7.00 MANN. Manual of Psychological Medicine. \$3.00 PERSHING. Diagnosis of Nervous and Mental Disease. Illustrated. REGIS. Mental Medicine. By H. M. BANNISTER, M.D. \$2.00 STEARNS. Mental Diseases. With a Digest of Laws Relating to Care of Insane. Illustrated. Cloth, \$2.75; Sheep, \$3.25 TUKE. Dictionary of Psychological Medicine. Giving the Definition of Terms and the Symptoms, Pathology. and Treatment of Mental Disorders. Iwo volumes. \$10.00 WOOD, H. C. Brain and Overwork.

CHEMISTRY AND TECHNOLOGY.

Special Catalogus of Chemical Books sent free upon application.

ALLEN. Commercial Organic Analysis. A Treatise on the Modes of Assaying the Various Organic Chemicals and Products Employed in the Arts. Manufactures, Medicine, etc., with Concise Methods for the Detection of Impurities, Adulterations, etc. 8vo.

Vol. I. Alcohols, Neutral Alcoholic Derivatives, etc., Ethers Vegetable Acids, Starch, Sugars, etc. 3d Edition. \$4.50

Vol. II, Part II. Fixed Oils and Fats, Glycerol, Explosives, etc. 3d Edition. William of Proceedings of the Commercial States, Bensenes, Naphthalenes and Derivatives, Creocote, Phenola, etc. 3d Edition. \$3.50

Vol. II, Part III. Terpenes, Essential Oils, Resins, Camphors, etc. 3d Edition. States, States, Camphors, etc. 3d Edition. Falarged and Rewritten. Illustrated. \$4.50

Vol. III, Part II. The Amines, Hydrasines and Derivatives, Pyridine Bases. The Antipyretics, etc. Vegetable Alkaloids, Tea, Coffee, Cocoa, etc. 8vo. 2d Edition. \$4.50

Vol. III, Part III. Vegetable Alkaloids, Non-Basic Vegetable Blitter Principles. Animal Bases, Animal Acids, Cyanogen Compounds, etc. 2d Edition, 8vo.

Vol. IV. The Proteids and Albuminous Principles. 2d Edition.

BAILEY AND CADY. Qualitative Chemical Analysis. \$1.25

BARTLEY. Medical and Pharmaceutical Chemistry. A Text-Book for Medical, Dental, and Pharmaceutical Students. With Illustrations, Glossary, and Complete Index. 5th Ed. \$3.00

BARTLEY. Clinical Chemistry. The Examination of Feces, Saliva, Gastric Juice, Milk, and Urine. New Edition. In Press.

BLOXAM. Chemistry, Inorganic and Organic. With Experiments. 9th Ed., Revised. 284 Engravings.

CALDWELL. Elements of Qualitative and Quantitative Chemical Analysis. 8d Edition, Revised. \$1.00

BROOMELL. Anatomy and Histology of the Human Mouth and Teeth. Second Edition, Revised and Enlarged. 337 handsome Illustrations. Cloth, \$4.50; Leather, \$5.50

FILLEBROWN. Operative Dentistry. Illustrated.

GORGAS. Dental Medicine. A Manual of Materia Medica and Therapeutica. 7th Edition. Cloth, \$4.00; Sheep,\$5.00

GORGAS. Questions and Answers for the Dental Student. Embracing all the subjects in the Curriculum of the Dental Student. Octavo. \$6.00

ARRIS. Principles and Practice of Dentistry. Including Anatomy, Physiology, Pathology, Therapeutics, Dental Sur-gery, and Mechanism. 13th Edition. Revised by F. J. S. Gorgas, M.B., B.B.S. 1250 Illus. Cloth, \$6.00; Leather, \$7.00 Including

HARRIS. Dictionary of Dentistry. Including Definitions of Such Words and Phrases of the Collateral Sciences as Pertain to the Art and Practice of Dentistry. 6th Edition, Revised and Enlarged by FERDINAND J. S. GORGAR, M.D., B.D.S. Cloth, \$5.00; Leather, \$6.00

CHARDSON. Mechanical Dentistry. 7th Edition. Thoroughly Revised and Enlarged by Dr. Gro. W. Warren. 691 Illustrations. Cloth, \$5.00; Leather, \$6.00 RICHARDSON.

SMITH. Dental Metallurgy. 2d Edition. Illustrated.

TAFT. Index of Dental Periodical Literature.

TOMES. Dental Anatomy. 263 Illustrations. 6th Ed. In Press.

TOMES. Dental Surgery. 4th Edition. 289 Illus. \$4 00

WARREN. Compend of Dental Pathology and Dental Medicine. With a Chapter on Emergencies. 4th Edition. Illustrated. \$1.00; Interleaved, \$1.25

WARREN. Dental Prosthesis and Metallurgy. 129 Illus. Edition, Enlarged and Revised. Nearly 1 Nearly Ready.

.40

WHITE. The Mouth and Teeth. Illustrated.

#### CYCLOPEDIAS. DICTIONARIES.

OULD. The Illustrated Dictionary of Medicine, Biology, and Allied Sciences. Being an Exhaustive Lexicon of Medicine and those Sciences Collateral to it: Biology (Zoology and Botany), Chemistry, Dentistry, Pharmacology, Microscopy, etc., with many useful Tables and nunerous fine Illustrations. 1633 pages. Fifth Edition.

, Sheep or Half Morocco, \$10.00; with Thumb Index, \$11.00 Half Russia, Thumb Index, \$12.00

OULD. The Medical Student's Dictionary. 11th Edition. Illustrated. Including those Words and Phrases generally used in Medicine, with their Proper Pronunciation and Definition, Based on Recent Medical Literature. With Table of Eponymic Terms and Tests and Tables of the Bacilli, Micrococci, Mineral Springs, etc., of the Arteries, Muscles, Nerves, Ganglia, Plexuses, etc. Eleventh Edition. Enlarged and illustrated with a legra number of Fagrayings. 840 pages. GOULD. with a large number of Engravings. 840 pages.

Half Morocco, \$2.50; with Thumb Index, \$3.00

Flexible Leather, Burnished Edges, Thumb Index, \$3.50

GOULD. The Pocket Pronouncing Medical Lexicon. 4th Edition. (30,000 Medical Words Pronounced and Defined.) Containing all the Words, their Definition and Pronunciation, that the Medical, Dental, or Pharmacoutical Student Generally Comes in Contact with; also Elaborate Tables of Eponymic Terms, Arteries Muscles, Nerves, Bacilli, etc., etc., a Dose List in both English and Metric Systems, etc., Arranged in a Most Convenient Form for Reference and Memorising. Fourth Edition, Revised and Enlarged. 838 pages.
Full Limp Leather, Gitt Edges, \$1.00; Thumb Index, \$1.25 165,000 Copies of Gould's Dictionaries have been sold.

165,000 Copies of Gould's Dictionaries have been sold.

GOULD AND PYLE. Cyclopedia of Practical Medicine and Surgery. Seventy-two Special Contributors. Illustrated. One Volume. A Concise Reference Handbook of Medicine, Surgery, Obstetrics, Materia Medica, Therapeutics, and the Various Specialties, with Particular Reference to Diagnosis and Treatment. Compiled under the Editorial Supervision of George M. Gould, M.D., Author of "An Illustrated Dictionary of Medicine," etc.; and Walter L. Pyls, M.D., Assistant Surgeon Wills Eve Hospital; formerly Editor "International Medical Magazine," etc., and Seventy-two Special Contributors. With many Illustrations. Large Square Svo, to correspond with Gould's "Illustrated Dictionary."

Full Sheep or Half Mor., \$10.00; with Thumb Index, \$11.00 net.

GOULD AND PYLE. Pocket Cyclopedia of Medicine and Sur-

GOULD AND PYLE. Pocket Cyclopedia of Medicine and Sur-gery. Based upon above book and uniform in size with gery. Based upon account of Gould's Pocket Dictionary."

Full Limp Leather, Gilt Edges, \$1.00

With Thumb Index, \$1.25

HARRIS. Dictionary of Dentistry. Including Definitions of Such Words and Phrases of the Collateral Sciences as Pertain to the Art and Practice of Dentistry. 6th Edition, Revised and Enlarged by Ferdinand J. S. Gorgas, M.D., D.B.S.

Cloth, \$5.00; Leather, \$6.00

LONGLEY. Pocket Medical Dictionary. Cloth, .75 TREVES AND LANG. German-English Medical Dictionary. Half Calf. \$3.25

#### DIET AND FOOD.

ALLEN. Proteids and Albuminous Principles. An analytical Study of Food Products. 2d Edition.

BURNETT. Foods and Dietaries. A Manual of Clinical Dietetics, with Diet Lists for Various Diseases, etc. 3d Ed. \$1.50

DAVIS. Dietotherapy. Food in Health and Disease. With Tables of Dietaries, Relative Value of Foods, etc. See Cohen, Physiologic Therapeutics, page 17.

GREENISH. Microscopical Examination of Foods and Drugs Illustrated.

HAIG. Diet and Food. Considered in Relation to Strength and Power of Endurance. 4th Edition. \$1.00

LEFFMANN. Select Methods in Food Analysis. 2d Edition. Illustrated.

#### EAR (see also Throat and Nose).

BURNETT. Hearing and How to Keep It. Illustrated. .40
HOVELL. Diseases of the Ear and Raso-Pharynz. Including
Anatomy and Physiology of the Organ, together with the
Treatment of the Affections of the Nose and Pharynx which
Conduce to Aural Disease. 128 Illustrations. 2d Ed. \$5.50
PRITCHARD. Diseases of the Ear. 4th Edition, Enlarged.
Many Illustrations and Formule. In Press.

#### ELECTRICITY.

BIGELOW. Plain Talks on Medical Electricity and Batteries. With a Therapeutic Index and a Glossary. 43 Illustrations. 2d Edition.

HEDLEY. Therapeutic Electricity and Practical Muscle Testing. 99 Illustrations. \$2.50

JACOBY. Electrotherapy. 2 volumes. Illustrated. See Cohen, Physiologic Therapeutics, page 17.

JONES. Medical Electricity. 3d Edition. 117 Illus. \$3.00

#### EYE.

A Special Circular of Books on the Eye sent free upon application. DARIER. Ocular Therapeutics. Just Ready. DONDERS. The Nature and Consequences of Anomalies of Refraction. With Portrait and Illus. Half Morocco, \$1.25 FICK. Diseases of the Eye and Ophthalmoscopy. Translated by A. B. Halm, M.D. 157 Illus. Cloth, \$4.50; Sheep, \$5.50 GOULD AND PYLE. Compend of Diseases of the Eye and Refraction. Including Treatment and Operations, and a Section on Local Therapeutics. With Formulæ, Useful Tables, a Glossary, and 111 Illus., several of which are in colors. 2d Edition, Revised. Cloth, \$1.00; Interleaved, \$1.25 GOWERS. Ophthalmoscopy. 4th Edition. Illus. In Press. GREEFF. The Microscopic Examination of the Eye. Illus-\$1.25 trated. HARLAN. Byesight, and How to Care for It. Illus. .40 HARTRIDGE. On the Ophthalmoscope. 4th Edition.
4 Colored Plates and 68 Wood-cuts. With \$1.50 4 Colored Flates and to wow.

HARTRIDGE. Refraction. 104 Illustrations and Test Types.

\$1.50 HANSELL AND SWEET. Treatise on Diseases of the Eye.
With 253 Illustrations. \$4.00 \$4.00 HANSELL AND REBER. Muscular Anomalies of the Eye.

Villustrated \$1.50 HENDERSON. Notes on the Eye. 138 Illus. 3d Ed. \$1.50 JENNINGS. Manual of Ophthalmoscopy. 95 Illustrations and 1 Colored Plate. MORTON. Refraction of the Eye. Its Diagnosis and the Correction of its Errors. 7th Edition.

OHLEMANN. Ocular Therapeutics. In Press Authorised Translation, and Edited by Dr. CHARLES A. OLIVER.

PARSONS. Elementary Ophthalmic Optics. With Diagrammatic Illustrations. \$2.00

PHILLIPS. Spectacles and Eyeglasses. Their Prescription and Adjustment. 3d Edition. 52 Illustrations. \$1.00

SWANZY. Diseases of the Rye and Their Treatment. 8th Edition, Revised and Enlarged. 168 Illustrations. 1 Plain Plate and a Zephyr Test Card.

THORINGTON. Retinoscopy. 4th Edition, Carefully Revised. Illustrated.

THORINGTON. Refraction and How to Refract. 200 Illustrations, 13 of which are colored. 2d Edition. \$1.50

WALKER. Studen' Ald in Ophthalmology. Colored Plate and 40 other Illustrations and a Glossary. \$1.50

WORTH. Squint: Its Causes, Pathology, Treatment. \$2.00

WRIGHT. Ophthalmology. 2d Edition, Revised and Enlarged. 117 Illustrations and a Glossary.

#### FEVERS.

GOODALL AND WASHBOURN. Fevers and Their Treatment. Illustrated. \$3.00
WILCOX. Fever Nursing. Just Ready. \$1.00

#### GYNECOLOGY.

BYFORD (H. T.). Manual of Gynecology. 3d Edition, Revised and Enlarged. 363 Illustrations. \$3.00; Sheep, \$3.50 FULLERTON. Surgical Nursing. 3d Edition, Revised and Enlarged. 69 Illustrations.

GALABIN. Diseases of Women. Sixth Edition. By Alfred and Enlarged. 284 Illustrations. Octavo. Cloth, \$5.00 LEWERS. Diseases of Women. 146 Illus. 5th Ed. \$2.50 MONTGOMERY. Practical Gynecology. A Complete Systematic Text-Book. 2d Edition, Revised and Enlarged. With 539 Illus. Cloth, \$5.00; Leasther, \$6.00 ROBERTS. Gynecological Pathology. With 127 Full-page Plates containing 151 Figures. \$6.00 WELLS. Compend of Gynecology. 145 Illustrations. 3d Edition, Revised and Enlarged. \$1.00; Interleaved, \$1.25

#### HEART.

THORNE. The Schott Methods of the Treatment of Chronic Heart Disease. Fourth Edition. Illustrated. \$2.00

#### HISTOLOGY.

CUSHING. Compend of Histology. By H. H. Cushine, M.D., Demonstrator of Histology, Jefferson Medical College, Philadelphia. Illus. Nearly Ready. \$1.00; Interleaved, \$1.25 LAZARUS-BARLOW. Pathelogical Anatomy and Histology. Illustrated. \$6.50

STIRLING. Outlines of Practical Histology. 368 Illustrations. 2d Edition, Revised and Enlarged. With new Illus. \$2.00 STÖHR. Histology and Microscopical Anatomy. Edited by A. SCHAPER, M.D., University of Breslau, formerly Demonstrator of Histology, Harvard Medical School. Fifth American from 10th German Edition, Revised and Enlarged. 353 Illustrations.

HYGIENE. CANFIELD. Hygiene of the Sick-Room. A Book for Nursee and Others. Being a Brief Consideration of Assessis, Antisepsis, Disinfection, Bacteriology, Immunity, Heating, Ventisepsis, Control of the State lation, etc. \$1.25 CONN. Agricultural Bacteriology. Illustrated. \$2.50 CONN. Bacteriology of Milk and Milk Products. Illus. \$1.25 COPLIN. Practical Hygiene. A Complete American Text-Book. 138 Illustrations. New Edition. Preparing. HARTSHORNE. Our Homes. Illustrated. KENWOOD. Public Health Laboratory Work. 116 Illustrations and 3 Plates. \$2.00 LEFFMANN. Select Methods in Food Analysis. 53 Illustra-tions and 4 Plates. 2d Edition. In Press. LEFFMANN. Examination of Water for Senitary and Technical Purposes. 5th Edition. Illustrated. Just Ready. \$1.25 LEFFMANN. Analysis of Milk and Milk Products. Illustrated. Second Edition. LINCOLN. School and Industrial Hygiene. McFARLAND. Prophylexis and Personal Hygiene. Care of the Sick. See Cohen, Physiologic Therapeutice, page 17. The Theory and Practice of Hygiene. 15 Plates and NOTTER. 138 other Illustrations. 8vo. 2d Edition. PARKES AND KENWOOD. Hygiene and Public Health.
Edition, Enlarged. Illustrated. \$3.00 ROSENAU. Disinfection and Disinfectants. Illus. \$2.00 STARR. The Hygiene of the Nursery. Including the General Regimen and Feeding of Infants and Children, and the Domestic Management of the Ordinary Emergencies of Early Life, Massage, etc. 6th Edition. 25 Illustrations.

STEVENSON AND MURPHY. A Treatise on Hygiene. By Various Authors. In three octavo volumes. Illustrated.

Vol. 1, 86.00; Vol. 11, 86.00; Vol. 111, 85.00 THRESH. Water and Water Supplies. 3d Edition. THRESH. Examination of Water and Water Supplies. In Press. WILSON. Handbook of Hygiene and Sanitary Science. With Illustrations. 8th Edition. \$3.00 WEYL. Sanitary Relations of the Coal-Tar Colors. Authorised Translation by HENRY LEFFMANN, M.D., PH.D.

#### LUNGS AND PLEURÆ.

KNOPF. Pulmonary Tuberculosis. Its Modern Prophylaxis and Treatment in Special Institutions and at Home. Illus. \$3.00 STEELL. Physical Signs of Pulmonary Disease. Illus. \$1.25

#### MASSAGE. PHYSICAL EXERCISE.

OSTROM. Massage and the Original Swedish Movements. Their Application to various Diseases of the Body. A Manual for Students, Nurses, and Physicians. Fifth Edition, Enlarged. 115 Illustrations, many of which are original. \$1.00

MITCHELL AND GULICK. Mechanotherapy. Exercise, Orthopedics, Massage, Ocular Corrections, etc. Illustrated. Sec. Cohen, Physiologic Therapsutics, below. Just Ready.

TREVES. Physical Education. Its Value, Methods, etc. .79

#### MATERIA MEDICA AND THERAPEUTICS.

BRACKEN. Outlines of Materia Medica and Pharmacology. \$2.75 COBLENTZ. The Newer Remedies. Including their Synonyms, Sources, Methods of Preparation, Tests, Solubilities, Doses, etc. 3d Edition, Enlarged and Revised. \$1.00

COHEM. Physiologic Therapeutics. Methods other than Drug-Giving useful in the Prevention of Disease and in the Treatment of the Sick. Mechanotherapy, Mental Therapeutics, Suggestion, Electrotherapy, Climatology, Hydrotherapy, Pneumatotherapy, Prophylaxis, Dietetics, Organotherapy, Phototherapy, Mineral Waters, Baths, etc. 11 volumes, 8vo. Illustrated. (Subscription.) Cloth, \$27.50; † Mor., \$38.50 Special Descriptive Circular will be sent upon application.

GORGAS. Dental Medicine. A Manual of Materia Medica and Therapeutics. 7th Edition, Revised. \$4.00

GROFF. Materia Medica for Nurses, with Questions for Self-Examination. 2d Edition, Revised and Improved. \$1.25

HELLER. Essentials of Materia Medica, Pharmacy, and Prescription Writing. \$1.50 HEWLETT. Serum-Therapy, Vaccines, etc. \$1.75

POTTER. Handbook of Materia Medica, Pharmacy, and Therapeutics, including the Action of Medicines, Special Therapeutics, Pharmacology, etc., including over 600 Prescriptions and Formulæ. 9th Edition, Revised and Enlarged. With Thumb Index in each copy. Cloth, \$5.00; Sheep, \$6.00

POTTER. Compend of Materia Medica, Therapeutics, and Prescription Writing, with Special Reference to the Physiological Action of Drugs. 6th Edition. \$1.00; Interleaved, \$1.25

Action of Drugs. 6th Edition. \$1.00; Interleaved, \$1.25
MURRAY. Rough Notes on Remedies. 4th Edition. \$1.25

SAYRE. Organic Materia Medica and Pharmacognosy. An Introduction to the Study of the Vegetable Kingdom and the Vegetable and Animal Drugs. Comprising the Botanical and Physical Characteristics, Source, Constituents, and Pharmacol Source, Constituents, and Pharmacol Botany. With sections on Histology and Microtechnique, by W. C. Stevens. 374 Illustrations, many of which are original. 3d Edition.

SCOVILLE. The Art of Compounding. 3d Edition, Revised and Enlarged. Just Ready. \$2.50

TAVERA. Medicinal Plants of the Philippines. \$2.00 WHITE AND WILCOX. Materia Medica, Pharmacy, Pharmacology, and Therapeutics. 5th American Edition, Revised by RHYNOLD W. WILCOX, M.A., M.D., LL.D., Professor of Clinical Medicine and Therapeutics at the New York Post-Graduate Medical School. Cloth, \$3.00; Leather, \$3.50

#### MEDICAL JURISPRUDENCE AND TOXICOLOGY.

EESE. Medical Jurisprudence and Toxicology. A Text-Book for Medical and Legal Practitioners and Students. 6th Edition. Revised by HEWEY LEFFMANN. M.D. Cloth, \$3.00; Leather, \$3.50

"To the student of medical jurisprudence and toxicology it is invaluable, as it is concise, clear, and thorough in every respect."

—The American Journal of the Medical Sciences.

Memoranda of Poisons. Their Antidotes and Tests. TANNER. 9th Edition, by Dr. HENRY LEFFMANN.

#### MICROSCOPY.

CARPENTER. The Microscope and Its Revelations, 8th Edition, Revised and Enlarged. 817 Illustrations and 23 Plates. Cloth, \$8.00; Half Morocco, \$9.00

GREENISH. Microscopical Examination of Foods and Drugs. Illustrated.

RE. The Microtomist's Vade Mecum. A Handbook of Methods of Microscopical Anatomy. 887 Articles. 5th Edition, Enlarged. \$4.00 LRR.

OERTEL. Medical Microscopy. A Guide to Diagnosis, Elementary Laboratory Methods and Microscopic Technic. 131 Illustrations. \$2.00 Illustrations.

REEVES. Medical Microscopy, including Chapters on Bacteriology, Neoplasms, Urinary Examination, etc. Numerous Illustrations, some of which are printed in colors. \$2.50

WETHERED. Medical Microscopy. A Guide to the Use of the Microscope in Practical Medicine. 100 Illustrations. \$2.00

#### MISCELLANEOUS.

\$4.00

BERRY. Diseases of Thyroid Gland. Illustrated. BUXTON. Anesthetics. Illustrated. 3d Edition. OHEN. Organotherapy. See Cohen, Physiologic Therapeutics, page 17. \$1.50 COHEN. FRENKEL. Tabetic Ataxia. Illustrated. GOULD. Borderland Studies. Miscellaneous Essays. 12mo. \$2.00

GOULD. Borderland Studies. Miscounier L. The Origin of the Ill-Health of DeQuincy, Carlyle, Darwin, Huxley, and \$1.00 Browning.

GOULD Biographic Clinics. Volume II. The Origin of the Ill-Health of Wagner, Parkman, Mrs. Carlisle, Spencer, Whittier, Ossoli, George Eliot, and Nietsche. \$1.00

Tilme-\$1.25

Their \$2.00

.40

REENE. Medical Examination for Life Insurance. Illus. With colored and other Engravings. 2d Edition. In Press. GREENE. HAIG. Causation of Disease by Uric Acid. The Pathology of High Arterial Tension, Headache, Epilepsy, Gout, Rheuma-tism, Diabetes, Bright's Disease, etc. 6th Edition. \$3.50 HENRY. A Practical Treatise on Anemia. OSGOOD. The Winter and Its Dangers. Half Cloth, .50 .40 OSLER. Essays and Addresses. In Press. PACKARD. Sea Air and Sea Bathing. .40 .40 RICHARDSON. Long Life and How to Reach It. ST. CLAIR. Compend of Medical Latin. 2d Edition. In Press. SCHEUBE, Diseases of Warm Countries. Illustrated. \$8.00 TISSIER. Pneumotherapy, Aerotherapy, Inhalation Methods. See Cohen, Physiologic Therapeutics, page 17. TURNBULL, Artificial Anesthesia. 4th Ed. Illus. \$2.50
WARDEN. The Paris Medical School. Paper, 75
WEBER AND HISSDALE. Climatology and Health Resorts.
Including Mineral Springs. 2 vols. Illustrated with Colored
Maps. See Cohen, Physiologic Therapeutics, page 17. WILSON. The Summer and Its Diseases. WINTERNITZ. Hydrotherapy, Thermotherapy, Phototherapy, Mineral Waters, Baths, etc. Illustrated. See Cohen, Physiologic Therapeutics, page 17.

#### NERVOUS DISEASES.

DERCUM. Rest, Suggestion, Mental Therapeutics. See Cohen, Physiologic Therapeutics, page 17. GORDINIER. The Gross and Minute Anatomy of the Central Nervous System. With 271 original colored and other Illus-trations. Cloth, \$6.00; Sheep, \$7.00 GOWERS. Syphilis and the Nervous System. GOWERS. Manual of Diseases of the Nervous System. A
Complete Text-Book. Revised, Enlarged, and in many parts
Rewritten. With many new Illustrations. Two volumes.
Vol. I. Diseases of the Nerves and Spinal Cord. 3d Edition,
Enlarged.
Vol. II. Diseases of the Brain and Cranial Nerves; Cleneral and
Functional Disease. 2d Ed. Cloth, \$4.00; Sheep, \$5.00 GOWERS. Epilepsy and Other Chronic Convulsive Diseases 2d Edition. \$3.00 GOWERS. Clinical Lectures. Illustrated. Second Series \$3.00 \$2.00 Just Ready. HORSLEY. The Brain and Spinal Cord, the Structure and Functions of. Numerous Illustrations. \$2.50 ORMEROD. Diseases of the Nervous System. 66 Wood En-\$1.00 gravings.

PERSHING. Diagnosis of Nervous and Mental Diseases.

RESTON. Hysteria and Certain Allied Conditions. Nature and Treatment. Illustrated.

WOOD. Brain Work and Overwork.

trated.

PRESTON.

#### NURSING (see also Massage).

Special Catalogue of Books for Nurses sent free upon application.

CARFIELD. Hygiene of the Sick-Room. A Book for Nurses and Others. Being a Brief Consideration of Asspais, Antisepsis, Disinfection, Bacteriology, Immunity, Heating and Ventilation, and Kindred Subjects for the Use of Nurses and Other Intelligent Women.

CUFF. Lectures to Rurses on Medicine. 4th Edition. \$1.25
DAVIS. Bandaging. Its Principles and Practice. 163 Original Illustrations.

FULLERTON. Obstatic Nursing. 6th Ed. 45 Illus. \$1.00
GROFF. Materia Medica for Nurses. With Questions for Salf-Examination. 2d Edition, Revised and Improved. \$1.25
HADLEY. General, Medical, and Surgical Nursing. A very Complete Manual, Including Sick-room Cookery.

\$1.25
HUMPHREY. A Manual for Nurses. Including General Anatomy and Physiology, Management of the Sick-room, etc. 24th Edition. 79 Illustrations.

STARR. The Hygiene of the Nursery. Including the General Regimen and Feeding of Infants and Children, and the Domestic Management of the Ordinary Emergencies of Early Life. Massage, etc. 6th Edition. 25 Illustrations.

TEMPERATURE AND CLINICAL CHARTS. See page 25.

VOSWINKEL. Surgical Nursing. Second Edition, Enlarged. 112 Illustrations.

\$1.00
WILCOX. Fever Nursing. Just Ready.

#### OBSTETRICS.

BDGAR. Text-Book of Obstetrics. By J. CLIFTON EDGAR, M.D., Professor of Obstetrics and Clinical Midwifery, Medical Department of Cornell University, New York City, etc. 1221 Illustrations. Just Ready. Cloth, \$6.00; Sheep, \$7.00 FULLERTON. Obstetric Nursing. 6th Ed. Illus. \$1.00 LANDIS. Compend of Obstetrics. 7th Edition, Revised by WM. H. WELLS, M.D., Demonstrator of Clinical Obstetrics, Jefferson Medical College. 52 Illus. \$1.00; Interleaved, \$1.25 WINCKEL. Text-Book of Obstetrics, Including the Pathology and Therapeutics of the Puerperal State. Illustrated. \$5.00

#### PATHOLOGY.

DANIEL. Laboratory Exercises in Tropical Medicine. 34.00
BLACKBURN. Autopsies. A Manual of Autopsies Designed for the Use of Hospitals for the Insane and other Public Institutions. Ten full-page Plates and other Illustrations. 31.25
COPLIN. Manual of Pathology. Including Bacteriology, Technic of Post-Mortems, Methods of Pathologic Research, etc. 330 Illustrations, 7 Colored Plates. 3d Edition. \$3.50

DA COSTA. Clinical Hematology. A Practical Guide to the Examination of the Blood. Six Colored Plates and 48 Illus- trations. Cloth, \$5.00; Sheep, \$6.00
LAZARUS-BARLOW. Pathological Anatomy. With 7 Colored Plates and 171 other Illustrations. \$6.50
LAZARUS-BARLOW. General or Experimental Pathology.  Illustrated. 2d Edition. Just Ready. \$6.50
MacLEOD. The Pathology of the Skin. Colored and other Illustrations. \$5.00
MARTIN. Manual of Pathology. Illustrated. Just Ready. \$4.00 ROBERTS. Gynecological Pathology. Illustrated. \$6.00
THAYER. Compend of Special Pathology. Illustrated. \$1.00; Interieaved, \$1.25
THAYER. Manual of General and Special Pathology. 131 Illustrations. 711 pages. 2d Edition. Full Limp Moroeco, Gilt Edges, Round Corners. \$2.50
VIRCHOW. Post-Mortem Examinations. 3d Edition75
WHITACRE. Laboratory Text-Book of Pathology. With 121

#### PHARMACY.

Special Catalogue of Books on Pharmacy sent free upon application.

COBLENTZ. Manual of Pharmacy. A Complete Text-Book by the Professor in the New York College of Pharmacy. 2d Ed., Revised and Enlarged. 437 Illus. Cloth, \$2.50; Sheep, \$4.50 COBLENTZ. Volumetric Analysis. Illustrated. \$1.25

BEASLEY. Book of 3100 Prescriptions. Collected from the Practice of the Most Eminent Physicians and Surgeons—English, French, and American. A Compendious History of the Materia Medica, Lists of the Doses of all the Officinal and Established Preparations, an Index of Diseases and their Remedies. 7th Edition. \$2.00

BEASLEY. Druggists' General Receipt Book. Comprising a Copious Veterinary Formulary, Recipes in Patent and Proprietary Medicines, Druggists' Nostrums, etc.: Perfumery and Cosmetics, Beverages, Dietetic Articles and Condiments, Trade Chemicals, Scientific Processes, and many Useful Tables. 10th Edition. \$2.00

BRASLEY. Pharmaceutical Formulary. A Synopsis of the British, French, German, and United States Pharmacopaiss. Comprising Standard and Approved Formulæ for the Preparations and Compounds Employed in Medicine. 12th Ed. \$2.00

GREENISH. Microscopical Examination of Foods and Drugs. Illustrated. \$3.50

ROBINSON. Latin Grammar of Pharmacy and Medicine. 4th Edition. With elaborate Vocabularies. Just Ready. \$1.50

Edition. With elaborate Vocabularies. Just Ready. \$1.00 SAYRE. Organic Materia Medica and Pharmacognosy. An Introduction to the Study of the Vegetable Kingdom and the Vegetable and Animal Drugs. Comprising the Botanical and Physical Characteristics, Source, Constituents, and Pharmacopeial Preparations, Insects Injurious to Drugs, and Pharmacoll Botany. With sections on Histology and Microtechnique, by W. C. STRYBMS. 374 Illustrations. Third Edition.

OVILLE. The Art of Compounding. Third Edition, vised and Enlarged. Just Beady. Cloth, SCOVILLE.

scoville. The art vised and Enlarged. Just Ready.

STEWART. Compend of Pharmacy, Based upon "Remington" Text-Book of Pharmacy," 5th Edition, Revised in Accordance with the U. S. Pharmacoposis, 1890. Complete Tables of Metric and English Weights and Measures.

\$1.00; Interleaved, \$1.25

UNITED STATES PHARMACOPCIA. 7th Decennial Revision. Cloth, \$2.50 (postpaid, \$2.77); Bheep, \$3.00 (postpaid, \$3.27); Interleaved, \$4.00 (postpaid, \$4.50); Printed on one side of page only, unbound, \$3.50 (postpaid, \$3.90).

Select Tables from the U. S. P. Being Nine of the Most Impor-tant and Useful Tables, Printed on Separate Sheets. .25

POTTER. Handbook of Materia Medica, Pharmacy, and Thera-peutics. 600 Prescriptions. 9th Edition. Cloth, \$5.00; Sheep, \$6.00

#### PHYSIOLOGY.

Practical Physiology. An Elementary Class Book. 62 Illustrations.

BRUBAKER. Text-Book of Physiology. Illus. Nearly Ready.
BRUBAKER. Compand of Physiology. 11th Edition, Revised
and Enlarged. Illustrated. \$1.00; Interleaved, \$1.25

JONES. Outlines of Physiology. 96 Illustrations.

KIRKES. Handbook of Physiology. 17th Authorized Edition.
Revised, Rearranged, and Enlarged. By Prof. W. D. HalliBURTON, of Kings College, London. 681 Illustrations, some of
which are in colors. Cloth, \$3.00; Leather, \$3.75

LANDOIS. A Text-Book of Human Physiology. Histology and Microscopical Anatomy, with Special Reference to the Requirements of Practical Medicine. 5th American, translated and edited from the last German Edition by A. P. BRUBARER, M.D., and A. A. ESHNER, M.D.

STARLING. Elements of Human Physiology. 100 Illus. \$1.00 STIRLING. Outlines of Practical Physiology. Including Chemical and Experimental Physiology, with Special Reference to Practical Medicine. 3d Edition. 289 Illustrations. \$2.00

TYSON. Cell Doctrine. Its History and Present State. \$1.50

#### PRACTICE.

Physiologic Therapeutics. The Treatment of Disease by Methods other than Drug-giving. See page 17.

FAGGE. Practice of Medicine. 4th Edition, by P. H. PYB-SMITH, M.B. 2 volumes. Vol. I, \$6.00; Vol. II, \$6.00

FOWLER. Dictionary of Practical M writers. An Encyclopsedia of Medicine Practical Medicine. By various Cloth, \$3.00; Half Morocco, \$4.00

÷.,

GOULD AND PYLE. Cyclopedia of Practical Medicine and Surgery. A Concise Reference Handbook, with particular Reference to Diagnosis and Treatment. Edited by DES. GOWLD and PYLE, Assisted by 72 Special Contributors. Illustrated, one volume. Large Square Octavo, Uniform with "Gould's Illustrated Dictionary."

Sheep or Half Mor., \$10.00; with Thumb Index, \$11.00
Half Russia, Thumb Index, \$12.00

**Complete descriptive circular free upon application.

GOULD AND PYLE'S Pocket Cyclopedia of Medicine and Surgery. Based upon the above and Uniform with "Gould's Pocket Dictionary." Full Limp Leather, Gilt Edges, Round Corners, \$1.00; with Thumb Index, \$1.25.

HUGHES. Compend of the Practice of Medicine. 6th Edition.

UGHES. Compend of the Practice of Medicine. 6th Edution, Revised and Enlarged.

Part I. Continued, Eruptive, and Periodical Fevers, Disease of the Stomach, Intestince, Peritoneum, Biliary Passages, Liver, Kidneys, etc., and General Diseases, etc.

Part II. Diseases of the Respiratory System, Circulatory System, and Nervous System; Diseases of the Blood, etc.

Price of each part, \$1.00; Interleaved, \$1.25

Physician's Edition. In one volume, including the above two parts, a Section on Skin Diseases, and an Index. 6th Revised Edition. 625 pp. Full Morocco, Gilt Edge, \$2.25

TAYLOR. Practice of Medicine. 6th Edition.

TYSON. The Practice of Medicine. By James Tyson, M.R., Professor of Medicine in the University of Pennsylvania. Complete Systematic Text-book, with Special Reference to Diagnosis and Treatment. 3d Edition, Enlarged and Revised. Colored Plates and 125 other Illustrations.

Clath. \$5.50: Leather, \$6.50

Cloth, \$5.50; Leather, \$6.50

FERWICK. Cancer of the Cancer

STOMACH. INTESTINES.

FERWICK. Cancer of the Stomach. Just Ready.

#BMMETER. Diseases of the Stomach. Their Special Pathology, Diagnosis, and Treatment. With Sections on Anatomy, Analysis of Stomach Contents, Diseases. Surgery of the Stomach, etc. 3d Edition, Revised. With 15 Plates and 41 other Illustrations, a number of which are in colors.

Cloth, \$6.00; Sheep, \$7.00

HEMMETER. Diseases of the Intestines. Their Special Pathology, Diagnosis, and Treatment. With Sections on Anatomy and Physiology, Microscopie and Chemic Examination of Intestinal Contents, Secretions, Feces and Urine, Intestinal Bacteria and Parasites, Surgery of the Intestines, Diseases of the Rectum, etc. With Full-page Colored Plates and many other Original Illustrations. 2 volumes. Octavo.

Price of each volume, Cloth, \$5.00; Sheep, \$6.00

#### SKIN.

BULKLEY. The Skin in Health and Disease. Illustrated. .40 CROCKER. Diseases of the Skin. Their Description, Pathology, Diagnosis, and Treatment, with Special Reference to the Skin Eruptions of Children. 3d Edition, Thoroughly Revised. With New Illustrations. Cloth, \$5.00; Sheep, \$6.00

MacLEOD. The Pathology of the Skin. Colored and other Illustrations.

SCHAMBERG. Diseases of the Skin. 3d Edition, Revised and Enlarged. 106 Illustrations. Cloth, \$1.00; Interleaved, \$1.25 VAB HARLINGER. On Skin Diseases. A Practical Manual of Diagnosis and Treatment, with Special Reference to Differential Diagnosis. 3d Edition, Revised and Enlarged. With Formula and 60 Illustrations, some of which are printed in colors.

## SURGERY AND SURGICAL DISEASES (see also Urinary Organs).

Diseases of the Thyroid Gland. Illustrated. BERRY. Surgical Diagnosis. In Press. Preparing. BINNIE. Operative Surgery. Illustrated. BURRELL AND BLAKE. Case Teaching in Surgery. Just BUTLIN. Operative Surgery of Malignant Disease. 2d Edition. Illustrated. Octavo. 34.50
CASPER AND RICHTER. Functional Kidney Diagnosis. 81.50
The Analysis and Practice. 162 Original DAVIS. Bandaging. Its Principles and Practice. 163 Original Illustrations \$1.50 DEAVER. Surgical Anatomy. A Treatise on Human Anatomy in its Application to Medicine and Surgery. With about 500 very handsome full-page Illustrations Engraved from Original Drawings made by special Artists from Dissections prepared for the purpose. Three volumes. Royal Square Octavo. By Subscription only. Now Ready.

Half Morocoo or Sheep, \$30.00; Half Russia, \$33.00 DEAVER. Appendicitis: its Symptoms, Diagnosis, Pathology, Treatment, and Complications. Elaborately Illustrated with Colored Plates and other Illus. 3d Edition. Nearly Ready DOUGLAS. Surgical Diseases of the Abdomen. Illustrated l-page Plates. Cloth, \$7.00; Sheep, \$8.00 by 20 Full-page Plates. DULLES. What to do First in Accidents and Poisoning. 5th Edition. New Illustrations. \$1.00 FULLERTON. Surgical Nursing. 3d Ed. 69 Illus. \$1.00 HAMILTON. Lectures on Tumors. 3d Edition. \$1.25 HEATH. Minor Surgery and Bandaging. 12th Edition, Revised and Enlarged. 195 Illus., Formulæ, Diet List, etc. \$1.50
HEATH. Clinical Lectures on Surgical Subjects. \$2.00 HORWITZ. Compend of Surgery and Bandaging. Including Minor Surgery, Amoutations, Fractures, Dislocations, Surgical Diseases, etc., with Differential Diagnosis and Treatment. 5th Edition, very much Enlarged and Rearranged. 167 Illus., 98 Formuls. JACOBSON. Operations of Surgery. 4th Ed., Enlarged. 550 Illua. Two volumes. Cloth, \$10.00; Leather, \$12.00 Illua. Two volumes. Cloth, \$10.00; Leather, \$12.00

KEAY. Medical Treatment of Gall-Stones. \$1.25

KEHR. Gall-stone Disease. Translated by WILLIAM WOTENERS SBTMOUR, M.B. \$2.50 MAKINS. Surgical Experiences in South Africa. 1899-1990. Illustrated. \$4.0
MAYLARD, Surgery of the Alimentary Canal. 97 Illustration
2d Edition, Revised. \$3.0 \$4.00

- MOULLIN. Text-Book of Surgery. With Special Reference to Treatment. 3d American Edition. Revised and edited by John B. Hamilton, M.B., LL.B., Professor of the Principles of Surgery and Clinical Surgery, Rush Medical College, Chicago. 623 Illustrations, many of which are printed in colors.

  Cloth, \$6.00; Leather, \$7.00
- VOSWINKEL. Surgical Nursing. Second Edition, Revised and Enlarged. 111 Illustrations. \$1.00
- WALSHAM, Manual of Practical Surgery. 8th Ed., Revised and Enlarged. 622 Engravings and 20 Skiagrams. 1227 pages. 34.50

#### TEMPERATURE CHARTS, ETC.

- GRIFFITH. Graphic Clinical Chart for Recording Temperature, Respiration, Pulse, Day of Disease, Date, Age, Sex, Occupation, Name, etc. Printed in three colors. Sample copies free. Put up in loose packages of fifty, 50 cts. Price to Hospitals, 500 copies, \$4.00; 1000 copies, \$7.50.
- EEEN'S Clinical Charts. Seven Outline Drawings of the Body on which may be marked the Course of Disease, Fractures, Operations, etc. Each Drawing may be had separately, twenty-five to pad, 25 cents.

#### THROAT AND NOSE (see also Ear).

- COHEN. The Throat and Voice. Illustrated. .4
- HALL. Diseases of the Nose and Throat. 2d Edition, Enlarged.
  Two Colored Plates and 80 Illustrations. \$2.75
- HOLLOPETER. Hay Fever. Its Successful Treatment. \$1.00
- KNIGHT. Diseases of the Throat. A Manual for Students. Illustrated. Just Ready. \$3.00
- EYLE (J. J.). Disease of the Ear, Nose, and Throat. A Compend for Students. Illustrated. \$1.00; Interleaved, \$1.25
- McBRIDE. Diseases of the Thront, Nose, and Ear. With Colored Illustrations from Original Drawings. 3d Ed. \$7.00
- POTTER. Speech and its Defects. Considered Physiologically, Pathologically, and Remedially. \$1.00

#### URINE AND URINARY ORGANS.

- CASPER AND RICHTER. Functional Kidney Diagnosis. \$1.50
- HOLLAND. The Urine, the Gastric Contents, the Common Poisons, and the Milk. Memoranda, Chemical and Microscopical, for Laboratory Use. Illustrated and Interleaved. 6th Edition.
- KLERN. Diabetes and Glycosuria. \$2.50

24 Illus MEMMINGER. Diagnosis by the Urine. 2d Edition. \$1.00 trations.

MORRIS. Renal Surgery, with Special Reference to Stone in the Kidney and Ureter and to the Surgical Treatment of Calculous Anuria. Illustrated. \$2.00

OULLIN. Enlargement of the Prostate. Radical Cure. 3d Edition. Illustrated. MOULLIN. Its Treatment and MOULLIN. Inflammation of the Bladder and Urinary Fever.

Octavo. TYSON. Bright's Disease and Diabetes. Including Articles on Ocular Manifestations by Prof. G. E. DE SCHWEINITS. Colored Plates and other Illustrations. 2d Edition. In Press.

TISON. Guide to Examination of the Urine. For the Use of Physicians and Students. With Colored Plate and Numerous Illustrations engraved on wood. 10th Edition, Revised, Enlarged, and partly Rewritten. With New Illustrations. Just Ready. \$1.50 \$1.00

VAN NUYS. Chemical Analysis of Urine. 39 Illus.

#### VENEREAL DISEASES.

GOWERS. Syphilis and the Nervous System. \$1.00 STURGIS AND CABOT. Student's Manual of Venereal Diseas \$1.25 7th Revised and Enlarged Edition. 12mc

#### VETERINARY.

BALLOU. Equine Anatomy and Physiology. 29 Graphic ns. \$1.00; Interleaved, \$1.25 Illustrations.

JACOBSON. The Operations of Surgery. W. H. A. Jacobson, F.R.C.S., Surgeon to Guy's Hospital; Consulting Surgeon Royal Hospital for Children and Women; and F. J. STEWARD, F.R.C.S., Assistant Surgeon Guy's Hospital. Fourth Edition—Revised, Enlarged, and Improved. 550 Illustrations. Two Volumes, Octavo, 1524 pages.

Cloth, \$10.00; Sheep, \$12.00

"The important anatomical points are clearly set forth, the conditions indicating or contraindicating operative interference are given, the details of the operations themselves are brought forward prominently, and frequently the after-treatment is considered. Herein is one of the strong points of the book."-New York Medical Journal.

"We know of no series of books issued by any house that so fully meets our approval as these? Quis-Compende?. They are well arranged, full and concise, and are really the best line of text-books that could be found for either student or practitioner."

—Southern Clinic.

## **BLAKISTON'S ?QUIZ-COMPENDS?**

The Best Series of Manuals for the Use of Students.

Price of each, Cloth, \$1.00. Interleaved, for taking Notes, \$1.25

These Compends are based on the most popular text-books and the lectures of prominent professors, and are kept constantly revised, so that they may thoroughly represent the present state of the subjects upon which they treat. The authors have had large experience as Quis-Masters and attaches of colleges, and are well acquainted with the wants of students. They are arranged in the most approved form, thorough and concise, containing nearly root illustrations and lithograph plates, inserted wherever they could be used to advantage. Can be used by students of any college. They contain information nowhere else collected in such a condensed, practical shape.

POTTER. HUMAN ANATOMY. Seventh Edition. 138 Illustrations and 16 Plates of Nerves and Arteries.

HUGHES. PRACTICE OF MEDICINE. Part I. Sixth Edition, Enlarged and Improved.

HUGHES. PRACTICE OF MEDICINE. Part II. Sixth Edition, Revised and Improved.

BRUBAKER. PHYSIOLOGY. Eleventh Edition. Illus.

LANDIS. OBSTETRICS, Seventh Edition. 52 Illus.

POTTER. MATERIA MEDICA, THERAPEUTICS, AND PRE-SCRIPTION WRITING. Sixth Revised Edition.

WELLS. GYNECOLOGY. Third Edition. 145 Illus.

GOULD AND PYLE. DISRASES OF THE EYE. Second Edition. Refraction, Treatment, Surgery, etc. 109 Illus.

HORWITZ. SURGERY. Including Minor Surgery, Bandaging, Surgical Diseases, Differential Diagnosis and Treatment. Fifth Edition. With 98 Formula and 71 Illustrations.

LEFFMANN. MEDICAL CHEMISTRY. Fourth Edition. Including Urinalysis, Animal Chemistry, Chemistry of Milk, Blood, Tissues, the Secretions, etc.

STEWART. PHARMACY. Fifth. Edition. Based upon Prof. Remington's Text-Book of Pharmacy.

BALLOU. EQUINE ANATOMY AND PHYSIOLOGY. 29 graphic Illustrations.

WARREN. DENTAL PATHOLOGY AND DENTAL MEDICINE. Fourth Edition, Illustrated.

HATFIELD. DISEASES OF CHILDREN. 3d Edition.

ST. CLAIR. Medical Latin. 2d Edition. In Press

SCHAMBERG. DISEASES OF THE SKIN. Third Edition, Revised and Enlarged. 106 Illustrations.

CUSHING. HISTOLOGY. Illustrated. In I

THAYER. SPECIAL PATHOLOGY. 34 Illustrations.

KYLE. DISEASES OF THE EAR. NOSE, AND THROAT. 85 Illustrations.

## DA COSTA

# Clinical Hematology

A Practical Guide to the Examination of the Blood by Clinical Methods. With Reference to the Diagnosis of Disease. With Colored Illustrations. Cloth, \$5.00

*** A new, thorough, systematic, and comprehensive work, its purpose being, first, to show how to examine the blood, and second, how to diagnose from such examination diseases of the blood itself and general diseases. The author's aim has been to cover not alone the field of original research, but to supply a book for the student, the hospital physician and the general practitioner. It will be found wanting in none of these respects.

## **THAYER**

## Manual of Pathology

#### GENERAL AND SPECIAL

Second Edition. 131 Illustrations. 711 Pages.
12mo. Full Limp Morocco, Gilt Edges,
Round Corners, \$2.50.

This book shows evidence of clinical as well as pathological knowledge. It is a practical, concise, up-to date manual by a teacher of experience.

# The Pocket Cyclopedia of Medicine and Surgery

Full Limp Leather, Round Corners, Gill Edges, \$1.00 With Thumb Index, \$1.25

Uniform with "Gould's Pocket Dictionary"

A concise practical volume of nearly 600 pages, containing a vast amount of information on all medical subjects, including Diagnosis and Treatment of Disease, with Formulas and Prescriptions, Emergencies, Poisons, Drugs and Their Uses, Nursing, Surgical Procedures, Dose List in both English and Metric Systems, etc.

## By Drs. Gould and Pyle

Based upon their large "Cyclopedia of Medicine and Surgery." 38 38 38

** This is a new book which will prove of the greatest value to students. It is to the broad field of general medical information what "Gould's Pocket Dictionary" is to the more special one of definition and pronunciation of words. The articles are concise but thorough, and arranged in shape for quick reference. In no other book can be found so much exact detailed knowledge so conveniently classified, so evenly distributed, so methodically grouped. It is Multum in Parvo. Sample Pages Free.

#### A NEW EDITION

## CROCKER ON THE SKIN

The Diseases of the Skin. Their Description, Pathology, Diagnosis, and Treatment, with Special Reference to the Skin Eruptions of Children. By H. RADCLIFFE CROCKER, M.D., Physician to the Department of Skin Diseases, University College Hospital, London. With new Illustrations.

# Third Edition, Rewritten and Enlarged OCTAVO. JUST READY; CLOTH, \$5.00

*,* This new edition will easily hold the high position given the previous printings. The author is a member of American, English, French, German, and Italian Dermatological Societies, and a recognized authority the world over.

# STURGIS—MANUAL OF VENEREAL DISEASES

By F. R. STURGIS, M.D., Sometime Clinical Professor of Venereal Diseases in the Medical Department of the University of the City of New York. Seventh Edition, Revised and in Part Rewritten by the Author and Follen Cabot, M.D., Instructor in Genito-Urinary and Venereal Diseases in the Cornell University Medical College. 12mo. 216 pages. Cloth, \$1.25

*** This manual was originally written for students' use, and is as concise and as practical as possible. It presents a careful, condensed description of the commoner forms of venereal diseases which occur in the practice of the general physician, together with the most approved remedies.

### FOR THE DISSECTING ROOM

## Holden's Anatomy—Seventh Edition 320 Illustrations

A Manual of the Dissections of the Human Body. By JOHN LANGTON, F.R.C.S. Carefully Revised by A. HEWSON, M.D., Demonstrator of Anatomy, Jefferson Medical College, Philadelphia, etc. 320 Illustrations. Two small compact volumes. 12mo.

Vol. I. Scalp, Face, Orbit, Neck, Throat, Thorax, Upper
Extremity. 435 pages. 153 Illustrations.
Oil Cloth, \$1.50

Vol. II. Abdomen, Perineum, Lower Extremity, Brain, Eye, Ear, Mammary Gland, Scrotum, Testes. 445 pages. 167 Illustrations.

Oil Cloth, \$1.50

Each volume sold separately.

### Hughes and Keith — Dissections Illustrated

A Manual of Dissections by ALFRED W. HUGHES, M.B., M.R.C.S. (Edin.), late Professor of Anatomy and Dean of Medical Faculty, King's College, London, etc., and ARTHUR KEITH, M.D., Joint Lecturer on Anatomy, London Hospital Medical College, etc. In three parts. With 527 Colored and other Illustrations.

- I. Upper and Lower Extremity. 38 Plates, 116 other Illustrations. Cloth, \$3.00
- II. Abdomen. Thorax. 4 Plates, 149 other Illustrations. Cloth, \$3.00
- III. Head, Neck, and Central Nervous System. 16
  Plates, 204 other Illustrations. Cloth, \$3.∞

Each volume sold separately.

** The student will find it of great advantage to have a "Dissector" to supplement his regular text-book on anatomy. These books meet all requirements, and as they can be purchased in parts as wanted, the outlay is small.

# EDGAR'S OBSTETRICS

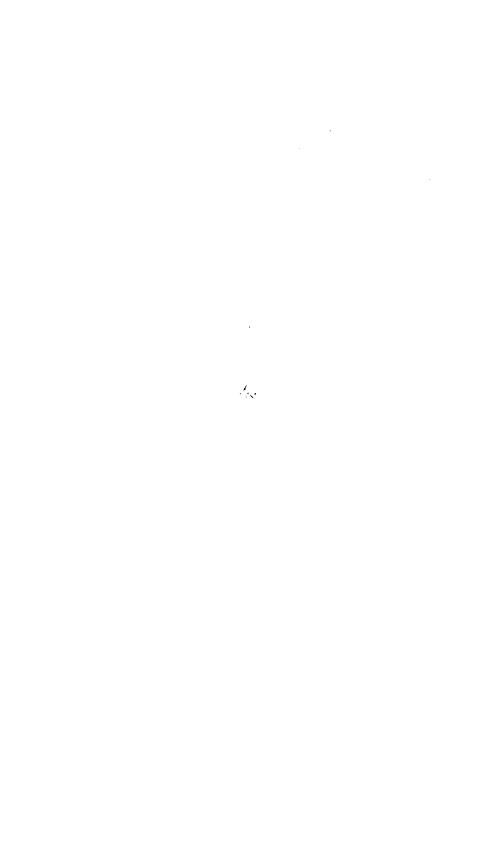
A NEW TEXT-BOOK

Edgar's Obstetrics excels all other works on this subject in completeness, in uniformity and consistency in arrangement, thoroughness and clearness in handling details, and in the number and usefulness of its illustrations. See page 20.

OCTAVO. CLOTH, \$6.00; SHEEP, \$7.00













11.

16 ch.



## THE NEW YORK PUBLIC LIBRARY REFERENCE DEPARTMENT

This book is under no circumstances to be taken from the Building

